(2) HT and the T-labeled form of the parent molecule irradiated account for 90% of the yield. HT is postulated to result from axial attack along the C–H bond, while displacement (without inversion) follows attack toward the central carbon atom. A crude quantitative formulation of the model which takes into account steric factors obstructing attack at certain angles accounts well for the observed ratio of HT to labeled parent.

(3) The detailed pattern of production of labeled alkanes is fully consistent with a mechanism involving displacement of an alkyl group by hot hydrogen attacking in a direction approximately normal to the C–C bond. As expected from steric considerations, alkyl displacement is less likely than H displacement despite the fact that the C–C bond is weaker than the C–H bond.

(4) Production of labeled radicals and alkenes is consistent with displacement of two groups or H atoms by the entering hot hydrogen. A mechanism involving dissociation of an excited labeled molecule formed by single hydrogen or alkyl group displacement is also possible. The radical formed may subsequently decompose to give a smaller radical and labeled alkene.

(5) Products which must be accounted for in terms of mechanisms additional to the simple displacement modes postulated (such as isomerization, break-up of highly excited species) amount to less than 0.5% of the total.

(6) The findings lend further support to a general model of hot hydrogen atom attack postulating a fast, direct displacement. The interval involved is of the order of 10^{-14} sec., the time required for one bond vibration, or for an H atom in the ev. range to traverse 10^{-8} cm. Formation of any metastable intermediate is very unlikely. Furthermore, because of the short duration of the collision and the small size of the hydrogen atom, energy is transferred only to the one or two bonds actually struck. This accounts for our observations that in nearly all of the initial displacements only one, or at most two, bonds are broken, and that the products of such reaction do not contain very large amounts of excitation. The fact that, despite the presence of very energetic hydrogen atoms, the yields of products having a very high energy of formation (e.g., allene from butane) is negligible, also becomes plausible. If the energetic hydrogen can only transfer energy to the immediate area of impact, the amount of energy thus transferred will not be sufficient to cause extensive decomposition.

In this fast displacement, considerations of energy economy are no longer of primary importance in determining the reaction path since ample energy is available for almost any process. Instead the bonds to be broken depend primarily on the point and direction of impact. (Energy factors only enter in determining which of the groups joined by the bond attacked is more likely to capture the hot atom.)

This model contrasts with the various formulations of thermal reactions in which statistical, quasi-equilibrium factors govern the decay of a well-defined intermediate. In hot displacement reactions many different "collision complexes" may be formed as is evident from the very high collision efficiencies observed.[3] But these "collision complexes" have a lifetime of less than one vibration; they are only locally excited and the geometry of their formation determines the products into which they pass. The connotation of the term "collision complex" is thus quite different from that normally assumed for thermal reactions. In hot processes it merely denotes that stage of the collision in which the participants are closest together. To emphasize the importance of the impact parameters of the collision in determining its result, we characterize this formulation of hot displacement reactions by the term "Impact Model."

Stereochemistry of Hot Hydrogen Displacement at sp³ Carbon–Hydrogen Bonds

By Michael Henchman[1] and Richard Wolfgang

The stereochemistry of the displacement of hydrogen by hot hydrogen atoms has been studied at an sp³ carbon atom in a gaseous molecule. The system used was the reaction of recoil tritium, from the nuclear reaction $He^3(n,p)H^3$, with optically active 2-butanol. There is $91 \pm 6\%$ retention of configuration for displacement of the hydrogen atom directly bonded to the asymmetric carbon. For the displacement of all the hydrogens throughout the molecule, there is $94 \pm 3\%$ retention of configuration. These results are well in accord with the model of hot hydrogen displacement postulating a fast, localized interaction occurring in about the characteristic period of a C–H bond vibration. According to such a model the short duration of the collision and the small size of the hydrogen atom allow no effective coupling mechanism for the concerted excitation of the several vibrational modes involved in the inversion process.

The reactions of high kinetic energy or "hot" atomic hydrogen, in the form of recoil tritium produced by nuclear reaction, have been the subject of several recent studies.[2-6] At thermal energies the sole reaction of hydrogen atoms with most saturated hydrocarbons is hydrogen atom abstraction.[7] With hot hydrogen, however, products appear of reactions other than abstraction. These reactions have been identified as a series of high energy displacement processes in which the hot hydrogen atom displaces a hydrogen atom, an alkyl group or possibly even two atoms or groups.[4,6]

Previous investigations have shown that these hot displacement reactions occur with high collision efficiency[4] at energies comparable to or higher than the activation energies of the reactions involved. Yield distributions indicate that the mechanism does not appear to involve a common intermediate, with lifetime long enough to permit internal equili-

(1) University Chemical Laboratory, Lensfield Road, Cambridge, England. Studies carried out in partial fulfillment of the requirements for the Ph.D. degree at Yale University.

(2) P. J. Estrup and R. Wolfgang, J. Am. Chem. Soc., 82, 2661, 2665 (1960).

(3) J. K. Lee, B. Musgrave and F. S. Rowland, ibid., 82, 3545 (1960).

(4) M. Henchman, D. Urch and R. Wolfgang, Can. J. Chem. 38, 1722 (1960).

(5) J. K. Lee, B. Musgrave and F. S. Rowland, ibid., 38, 1756 (1960).

(6) D. Urch and R. Wolfgang, J. Am. Chem. Soc., 83, 2982, 2997 (1961).

(7) R. Klein, J. R. McNesby, M. D. Scheer and L. J. Schoen, J. Chem. Phys., 30, 58 (1959).

bration of energy and decaying to the several products found.[2,6] Furthermore, because of the large amounts of energy available, considerations of energy economy do not seem to dominate the choice of the path of the reaction as is true for thermal energies. Thus displacement of hydrogen involving rupture of the strong C–H bond is more common than displacements in which the weaker C–C bond is broken.

If energy considerations do not determine the reaction path in hot reactions, the stereochemistry of the process should be of paramount importance in the understanding of their mechanism. This study reports on an investigation of the steric aspect of the process in which hot hydrogen displaces another hydrogen atom. For hydrocarbons this is the principal reaction peculiar to the high energy region.

Three limiting cases of the stereochemistry of the displacement might be considered to be possible: direct displacement, in which the hot hydrogen collides directly with the hydrogen and displaces it without disturbing the configuration of the rest of the molecule; displacement with Walden inversion, where the hot atom approaches the carbon atom along the axis of the carbon–hydrogen bond but from the opposite side of the carbon atom; displacement via a metastable intermediate, whereby the hot atom collides with the carbon and a hydrogen atom is subsequently lost. Thus in the displacement of a hydrogen bonded directly to an asymmetric carbon atom, the first mechanism would lead to retention of configuration, the second to inversion and the third to racemization.

Previous investigations of the stereochemistry of this high energy displacement have been confined to the solid phase. For the cases of glucose[3] and l-alanine,[9] the configuration was retained. Yet while these results are indicative, they cannot be directly applied to the gas phase for it could always be argued that, in the solid phase, the crystal structure would not allow any inversion. Furthermore, while hot reactions in the solid phase seem to occur by the same displacement processes found in the gas phase,[10] complications such as "cage effects" play some part.

Choice of System.—The system chosen for study was the displacement of the hydrogen atom bonded to the asymmetric carbon in optically active 2-butanol.

$$T^* + C_2H_5CHOHCH_3 \longrightarrow C_2H_5CTOHCH_3 + H$$
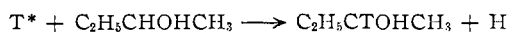
The high kinetic energy tritium was generated by neutron irradiation of He^3 mixed with the gaseous alcohol. This technique using the nuclear process $He^3(n,p)H^3$ is a familiar one and the system appears well defined.[2] The tritium is initially produced as a 190 Kev. ion, but by the time it has reached energies sufficiently low so it may become chemically bound ($< 10^2$ e.v.), it is an atom,

probably in its ground state.[11] Any atoms reaching thermal energies uncombined were eliminated by a small amount of added iodine. Thus only the products of hot reaction were observed.

Several factors dictated the choice of 2-butanol as the appropriate asymmetric molecule. (1) A system involving an sp^3 carbon atom was required. As shown in the following paper, hydrogen replacement at an sp^2 carbon is complicated by an addition reaction which may give the same product as the direct displacement[12] and by possible rotation about the double bond after the displacement. (2) A non-cyclic system was essential. Whereas such a system would permit ready separation of its geometrical isomers, its cyclic nature would impose a constraint on a possible mechanism involving inversion. (3) The compound had to have an appreciable vapor pressure at the temperature available in the high neutron flux facility of the Brookhaven reactor ($< 60°$).

The choice of 2-butanol had the disadvantage that both optical isomers could not be readily obtained pure. Fractional crystallization of the brucine salt of 2-butanol hydrogen phthalate will yield the pure dextro isomer, but recovery of the levo isomer from the mother liquors will only yield an optical purity of some 80–90% and then only from larger quantities of starting material than the activities obtainable here would allow.

Experimental Procedure

The experimental procedure is shown schematically in Fig. 1. Quartz ampoules, containing optically active 2-butanol, iodine and helium-3, were irradiated with slow neutrons. The tritiated 2-butanol was separated and purified by gas chromatography and tritium in its hydroxyl group was removed by vapor phase exchange with cotton. Following addition of a thousandfold excess of racemic carrier the sample was resolved to give three portions, dextro, levo and racemic. The specific activities of these 2-butanol portions were measured by both gas flow proportional counting and liquid scintillation counting. The ratios of the specific activities of these three portions then were used to calculate the extent of retention of configuration in the displacement of *any* non-labile hydrogen in the 2-butanol.

To obtain the retention of configuration in the displacement of the hydrogen at the asymmetric carbon, it was necessary to isolate this particular hydrogen atom.

The only degradation that seemed to allow direct counting of the tritium bonded to the asymmetric carbon atom was an Oppenauer oxidation, in which the 2-butanol would be oxidized to butanone by an aldehyde or ketone, being itself reduced to the corresponding carbinol. This aikoxide catalyzed equilibrium has been shown to involve a hydride ion transfer,[13] in which the hydrogen bonded to the asymmetric carbon of the 2-butanol is transferred directly to the carbinol carbon of the oxidant,[14] one molecule of carbinol being produced for every molecule of 2-butanol oxidized. If the oxidant ketone or aldehyde can enolize, then under the basic conditions present, it will exchange with the enolized butanone and the resulting carbinol will contain tritium that is not bonded to the carbinol carbon. Benzophenone cannot enolize and for this reason was used as the oxidant.

For the oxidation to be specific, the alkoxide alcohol must itself be incapable of oxidation; thus aluminum *t*-butoxide was used as the catalyst. This specificity was demonstrated by blank runs in which no benzhydrol was produced in the absence of 2-butanol.

(8) F. S. Rowland, C. N. Turton and R. Wolfgang, *J. Am. Chem. Soc.*, **78**, 2354 (1956); H. Keller and F. S. Rowland, *J. Phys. Chem.*, **62**, 1373 (1958).

(9) J. G. Kay, R. P. Malsan and F. S. Rowland, *J. Am. Chem. Soc.*, **81**, 5050 (1959).

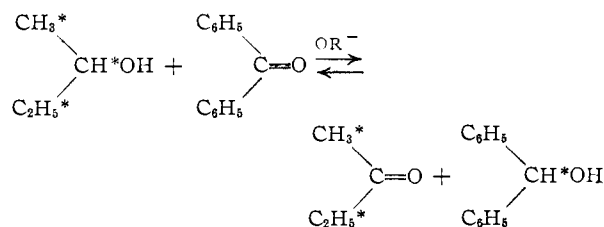(10) A. M. Elatrash, R. H. Johnsen and R. Wolfgang, *J. Phys. Chem.*, **64**, 785 (1960).

(11) M. Amr El-Sayed, P. J. Estrup and R. Wolfgang, *ibid.*, **62**, 1356 (1958).

(12) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **81**, 2025 (1959).

(13) W. von E. Doering and T. C. Aschner, *ibid.*, **75**, 393 (1953).

(14) E. D. Williams, K. A. Krieger and A. R. Day, *ibid.*, **75**, 2104 (1953).

$$CH_3^*\!\!\diagdown\!\!CH^*OH + C_6H_5\!\!\diagdown\!\!C{=}O \quad \overset{OR^-}{\rightleftharpoons}$$
$$C_2H_5^*/\qquad\qquad C_6H_5/$$

$$CH_3^*\!\!\diagdown\!\!C{=}O + C_6H_5\!\!\diagdown\!\!CH^*OH$$
$$C_2H_5^*/\qquad\qquad C_6H_5/$$

(Tritium introduced into the hydroxyl group of the benzhydrol by exchange with enolized butanone was removed during the aqueous extraction of the benzhydrol from the reaction mixture. Further exchange with water caused no reduction in its specific activity.)

Ratios of the specific activities of the benzhydrol portions were used to compute the extent of retention of configurations in the displacement of the hydrogen atom at the asymmetric carbon.

Experimental Details

Irradiation of the Optically Active 2-Butanol.—*d*-2-Butanol of 98% optical purity and *l*-2-butanol of 79% optical purity were separated from racemic 2-butanol by the procedures described below. Isomeric compositions of all samples throughout this work were determined by measurements of optical rotation; the specific rotation of pure *d*-2-butanol being taken as $[\alpha]^{20}\text{D} +13.83°$.[15]

The helium-3 (Oak Ridge National Laboratory) was purified by passage through a liquid nitrogen cooled charcoal trap. Its purity was checked by gas chromatography, mass spectrometry and (for tritium contaminant) by flow counting.[16]

Cylindrical quartz ampoules, with break-off tip, were filled on a vacuum line with helium-3 and sufficient optically active 2-butanol just to maintain its vapor pressure at 60° (150 mm.). Two or three crystals of iodine were added as scavenger to remove any thermalized tritium atoms and reactive species from radiation damage. Extreme irradiation conditions in the Brookhaven Reactor—maximum sample volume, high flux—were used to maximize the activity whilst keeping radiation damage below 20%. These conditions are listed in Table I. Unlike the dextro sample,

TABLE I
IRRADIATION CONDITIONS

	Dextro sample	Levo sample
Ampoule volume (ml.)	~50	~20
Mass of 2-butanol (mg.)	28	11
Helium-3 (cm. Hg. ml.)	~50	~20
Neutron flux (n./cm.²/sec.)	5×10^{12}	1.5×10^{13}
Time (min.)	60	30
Ampoule temp. on insertion	25°	100°

the levo was preheated to 100° before the irradiation, thereby ensuring that the 2-butanol was in the gas phase throughout. However, even the dextro sample will have been in the vapor phase for at least 90% of the irradiation.

Purification of the Tritiated 2-Butanol.—After irradiation, the ampoule and a sealed tube containing 10 λ *dl*-2-butanol carrier were broken under vacuum. The 2-butanol was purified by repeated passage through a combined gas chromatography-proportional counter unit, which simultaneously assayed both mass and radioactivity.[16] Column: 5 ft. × ¼ in. o.d. copper tubing containing bis-(2-(2-methoxyethoxy)-ethyl) ether, 40% on firebrick (30–60 mesh) at 100°; counter temperature, 110°; helium pressure, 3 lb./sq. in.

The labile tritium in the hydroxy group of the pure 2-butanol was removed by passing it in a stream of dry nitrogen through a cotton column at 120°: column, 10 ft. × ¼ in. o.d. copper tubing containing cotton, washed in methanol and dried. This technique is fully described elsewhere.[17] The "scrubbed" 2-butanol then was chromato-

(15) J. Kenyon. H. Phillips and V. P. Pitman. *J. Chem. Soc.*, **137**, 1077 (1935). The results of this paper might be interpreted as evidence that this value is too low. We have shown that this is not so, by measuring the specific rotation of pure *d*-2-butanol to be $[\alpha]\text{D}^{21} +13.8 \pm 0.5°$ by the method of isotope dilution.

(16) R. Wolfgang and F. S. Rowland. *Anal. Chem.*, **30**, 903 (1958).

$$CH_3\!\!\diagdown\!\!CHOH$$
$$C_2H_5/$$
Irradiated either *d* or *l*
isomer with hot tritium

Purify by gas chromatography
$$CH_3^*\!\!\diagdown\!\!CH^*OH^*$$
$$C_2H_5^*/$$
Remove hydroxyl tritium
by exchange with cotton

$$CH_3^*\!\!\diagdown\!\!CH^*OH$$
$$C_2H_5^*/$$
Add excess *dl* carrier

Resolve

d portion	*dl* portion	*l* portion
$CH_3^*\!\!\diagdown\!\!CH^*OH$ $C_2H_5^*/$	$CH_3^*\!\!\diagdown\!\!CH^*OH$ $C_2H_5^*/$	$CH_3^*\!\!\diagup\!\!CH^*OH$ $C_2H_5^*/$
Remove hydrogen at asymmetric carbon by Oppenauer oxidation	Remove hydrogen at asymmetric carbon by Oppenauer oxidation	Remove hydrogen at asymmetric carbon by Oppenauer oxidation
$C_6H_5\!\!\diagdown\!\!CH^*OH$ $C_6H_5/$	$C_6H_5\!\!\diagdown\!\!CH^*OH$ $C_6H_5/$	$C_6H_5\!\!\diagdown\!\!CH^*OH$ $C_6H_5/$

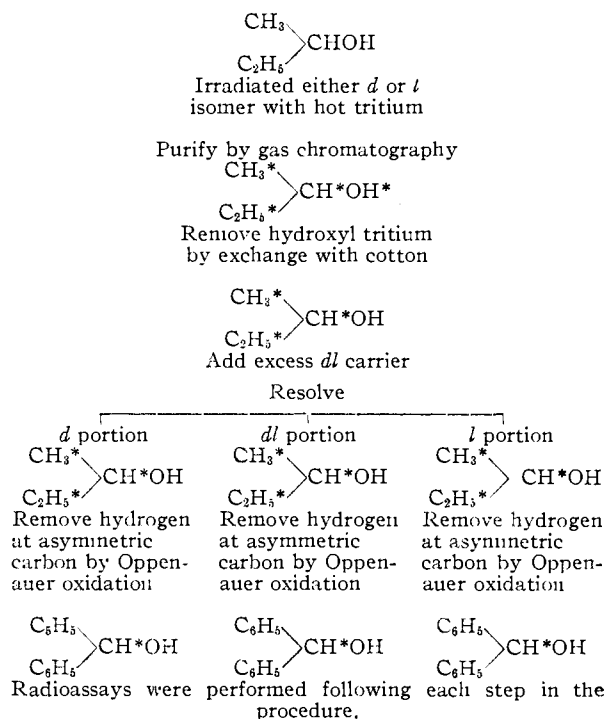Radioassays were performed following each step in the procedure.

Fig. 1.—The experimental procedure.

graphed and counted as before. The cotton column was decontaminated by passing water vapor through it in the reverse direction until the gas showed no activity. Repetition of the "scrubbing" resulted in an activity of <200 d.p.m. on the cotton column, thereby showing that the exchange was essentially complete after one "scrubbing." Total sample activities after "scrubbing" were dextro ~4 × 10⁶ d.p.m., levo ~1.6 × 10⁶ d.p.m.

Carrier Addition and Resolution.—The "scrubbed" 2-butanol was distilled into 10 ml. of *dl*-2-butanol carrier; 1 ml. of this was reserved for Oppenauer oxidations and specific activity determinations of the *dl* portion. The remainder was partially resolved into a dextro and a levo portion by fractional crystallization of the brucine salt of the 2-butanol hydrogen phthalate, using the procedure of Kantor and Hauser.[18] 8.5 g. of the less soluble dextro salt was obtained at ~97% optical purity; 8.5 g. of the levo salt was obtained at ~70% optical purity, by working up the mother liquors. These were hydrolyzed by distillation from a solution of the salt in 30 ml. of diethylene glycol, containing 3 g. of potassium hydroxide, followed by ethereal extraction of the 2-butanol, purification by gas chromatography (as before) and drying over calcium hydride (shown not to cause racemization). Yield was ~1.0 ml.

This same resolution procedure was used to obtain the sample of optically active 2-butanol that was irradiated. Here use of larger quantities gave a levo portion of ~80% optical purity.

Oppenauer Oxidation and Specific Activity Determinations.—The reaction mixture, containing 1.0 g. of benzophenone (Matheson) and 0.10 ml. of the 2-butanol in 2 ml. of a solution of aluminum *t*-butoxide (Matheson) in dry toluene (25 g./100 ml.), was stirred magnetically in a sealed tube at 100 ±5° for 30 hr. This was subsequently hydrolyzed by refluxing with 0.2 ml. of water for 30 minutes and the aluminum hydroxide was removed by centrifuging. Evaporation of the residual solution under reduced pressure left a glue, in which crystals formed at 5° if seeded with a crystal of benzophenone. The solid was crushed to a fine powder and stirred overnight with 400 ml. of distilled water at 5°. The benzophenone was filtered off and the benzhydrol extracted from the filtrate with chloroform, evaporated to dryness and recrystallized twice from heptane; yield 60–90 mg.; m.p., 66.5–68°. The analysis was

(17) M. Henchman, Ph.D. Thesis, Yale University, 1960.

(18) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 1744 (1953).

carried out in triplicate on three aliquots of each portion of 2-butanol.

The accurate measurements of the specific activities of the 2-butanol and benzhydrol were made with a liquid scintillation counter (Technical Measurements Co.), operating at 18% efficiency, with a low background quartz vial and 15 ml. standard scintillator solution, 4.0 g. of PPO and 0.05 g. of POPOP/liter toluene (Pilot Chemicals Inc.). The necessary correction was made for the quenching of the benzhydrol.

Results

Data Obtained.—Two samples of optically active 2-butanol, a dextro sample ($\sim$98% d) and a levo sample ($\sim$80% l), were subjected to the Experimental procedure. Tables II and III list the specific

TABLE II
RESULTS FOR THE DEXTRO SAMPLE

	Irradiated sample (x)	Isolated d portion (z_d)	Isolated l portion (z_l)
Fraction d-2-butanol	0.979 ± 0.003	0.968 ± 0.003	0.343 ± 0.002

Specific activities of the 2-butanol[a]

Portion	D.p.m./millimole L.s.c.	D.p.m./millimole G.f.p.c.	Apparent percentage at asymmetric carbon
Dextro	9900 ± 150	55300 ± 5000	9.1 ± 0.5
Racemic	5750 ± 150	34600 ± 3500	9.6 ± .4
Levo	4020 ± 120	23900 ± 2500	9.5 ± .7

Specific activities of the benzhydrol

	Yield in mg.	D.p.m./millimole (l.s.c.)	
Dextro portion	49	940 ± 25	
	76	850 ± 15	900 ± 25
	78	900 ± 20	
Racemic portion	81	555 ± 15	
	77.5	540 ± 15	550 ± 15
Levo portion	68	435 ± 10	
	65.5	365 ± 10	400 ± 30
	70	410 ± 10	

Ratios of specific activities

	2-Butanol L.s.c.	2-Butanol G.f.p.c.	Benzhydrol L.s.c.
$R_{d/dl}$	1.72 ± 0.09	1.6 ± 0.2	1.65 ± 0.08
$R_{l/dl}$	0.70 ± .04	0.7 ± .1	0.73 ± .05
$R_{d/l}$	2.47 ± .13	2.3 ± .2	2.25 ± .18

[a] l.s.c., liquid scintillation counting and g.f.p.c., gas flow proportional counting.

activities of the benzhydrol and the 2-butanol for the d, l and dl portions of each of the two samples. (Because of the low activities, the specific activity determinations of the 2-butanol fractions by gas flow proportional counting were subject to considerable random error; these values were not used in subsequent calculations and merely served as a check on the more accurate values obtained by liquid scintillation counting.) For each sample, values of the ratio R of the specific activities of the various portions, d/dl, l/dl and d/l were obtained for both benzhydrol and 2-butanol. R is directly related to the percentage of displacements causing retention of configuration about the asymmetric carbon by an expression derived below. Since this percentage depends upon a ratio, it is independent of the isotope effect in the Oppenauer oxidation; any systematic errors in the specific activity determinations will also be eliminated.

The benzhydrol results show some scatter, both in yield and specific activity. The scatter in yield, however, does not correspond to a similar scatter in specific activity. Thus the variation in benzhy-

TABLE III
RESULTS FOR THE LEVO SAMPLE

	Irradiated sample (1 − x)	Isolated d-portion (1 − z_d)	Isolated l-portion (1 − z_l)
Fraction l-2-butanol	0.786 ± 0.003	0.020 ± 0.002	0.666 ± 0.003

Specific activities of the 2-butanol

Portion	D.p.m./millimole L.s.c.	D.p.m./millimole G.f.p.c.	Apparent percentage at asymmetric carbon
Levo	3330 ± 50	21200 ± 2000	11.1 ± 0.6
Racemic	2850 ± 50	14900 + 1500	11.6 ± .4
Dextro	1400 ± 30	7700 ± 800	11.1 ± .5

Specific activities of the benzhydrol

	Yield in mg.	D.p.m./millimole (l.s.c.)	
Levo portion	66	345 ± 10	
	89.5	360 ± 10	365 ± 20
	70	395 ± 10	
Racemic portion	59	340 ± 10	
	64	320 ± 10	330 ± 10
	66.5	335 ± 10	
	71	155 ± 10	
Dextro portion	70	155 ± 10	155 ± 5
	70.5	160 ± 10	

Ratios of specific activities

	2-Butanol L.s.c.	2-Butanol G.f.p.c.	Benzhydrol
$R_{d/dl}$	0.49 ± 0.02	0.5 ± 0.1	0.47 ± 0.02
$R_{l/dl}$	1.17 ± .03	1.4 ± .2	1.11 ± .08
$R_{d/l}$	0.41 ± .02	0.35 ± .05	0.42 ± .03

drol yield indicates poor reproducibility in the aqueous extraction of the benzhydrol rather than in the approach to completion of the Oppenauer oxidation. That equilibrium had been reached in the Oppenauer oxidations was established by tripling the oxidation time and showing that there was no appreciable increase in the specific activity of the benzhydrol. Adkins' values for the carbinol-carbonyl oxidation potentials[19] indicate that some 80% of the 2-butanol should have been oxidized; the largest yield of benzhydrol corresponded to 50% oxidation; it seems likely that this discrepancy reflects the inefficiency of the benzhydrol extraction.

The variation in the benzhydrol specific activities probably can be attributed to the liquid scintillation counting of these samples of very low activity. The listed errors are merely those due to the statistics of the counting and take no account of slight changes in the machine's efficiency.

The apparent percentage of the total displacements of non-labile hydrogen that occur at the asymmetric carbon is found by dividing the benzhydrol specific activity by the 2-butanol specific activity. The constancy of this value for the three portions of each sample (dextro, 9.1–9.6%; levo, 11.1–11.6%) is a measure of the self-consistency of the l.s.c. specific activity determinations. The difference for the two samples irradiated is however well outside the expected error; fortunately it is irrelevant to the conclusions of this study. (It must be noted that the average of 10.4% for the percentage of hydrogen displacement at the asymmetric center is only an apparent value because of probable isotope effects in the Oppenauer oxidation and the subsequent extraction. Since the recovery of benzhydrol was only

(19) H. Adkins, R. M. Elofson, A. G. Rossow and C. G. Robinson, J. Am. Chem. Soc., 71, 3622 (1949).

50% of theoretical, this isotope effect may be as high as a factor of 2. Again, this does not affect the conclusions reached here.)

The Expression for the Fraction of Displacements Causing Retention of Configuration.—Let the irradiated optically active 2-butanol contain a fraction "x" of the dextro isomer and $(1 - x)$ of the levo. Let a fraction "y" of the hydrogen displacement reactions cause retention of configuration about the asymmetric carbon; and let $(1 - y)$ cause inversion.

In the tritiated 2-butanol, the fraction of the total activity in each isomer then is

dextro: $xy + (1 - x)(1 - y) = 1 - x - y + 2xy$

levo: $x(1 - y) + (1 - x)y = x + y - 2xy$

Excess dl-2-butanol is then added to make the gross composition of the sample racemic. It is then resolved to give a dextro and a levo portion, containing fractions "z_d," "z_l" of the dextro isomer and $(1 - z_d)$, $(1 - z_l)$ of the levo isomer, respectively. If the specific activities of the partially resolved dextro and levo portions are, respectively, $R_{d/dl}$ and $R_{l/dl}$ times the specific activity of the unresolved racemic 2-butanol, then:

$$R_{d/dl} = 2[z_d(1 - x - y + 2xy) + (1 - z_d)(x + y - 2xy)]$$
$$= 2[x + y + z_d - 2(xy + yz_d + z_dx) + 4xyz_d]$$

$$R_{l/dl} = 2[x + y + z_l - 2(xy + yz_l + z_lx) + 4xyz_l]$$

$$R_{d/l} = \frac{x + y + z_d - 2(xy + yz_d + z_dx) + 4xyz_d}{x + y + z_l - 2(xy + yz_l + z_lx) + 4xyz_l}$$

The quantities x, z_d and z_l are available from the specific rotations of the various portions and R from their specific activities (see Tables II and III). The above expressions are then solved for y.

The Percentage Retention of Configuration.—The percentage retention of configuration in the displacement reaction, "y," is listed in Table IV.

TABLE IV

PERCENTAGE RETENTION FOR HYDROGEN DISPLACEMENT AT ASYMMETRIC CARBON

	d/dl	l/dl	d/l
Dextro sample	86 ± 5	95 ± 8	90 ± 4
Levo sample	98 ± 4	80 ± 2	95 ± 3

PERCENTAGE RETENTION FOR HYDROGEN DISPLACEMENT THROUGHOUT MOLECULE

	d/dl	l/dl	d/l
Dextro sample	90 ± 5	100 ± 7	88 ± 10
Levo sample	96 ± 2	95 ± 7	96 ± 2

The values of R for 2-butanol (Tables II and III) were used to calculate "y" for retention of configuration throughout the whole molecule and those for benzhydrol yielded "y" for replacement at the asymmetric carbon only. The errors listed in Table IV correspond to errors in "R," which greatly exceed those in "x" and "z." An arithmetical mean of the values for the percentage retention is 91 ± 6% for displacement at the asymmetric carbon and 94 ± 3% for displacement throughout the molecule. These values are relatively insensitive to the value chosen for the specific rotation of pure d-2-butanol; an increase in this of 0.5° changes them to 93 ± 7% and 97 ± 3%, respectively.

If displacement at the asymmetric carbon causes less than 10% inversion, it would be expected that displacement in the methyl and ethyl groups should cause no inversion whatever about the asymmetric carbon. The apparent 6% inversion observed for displacement throughout the molecule may thus be a good measure of the actual accuracy of the experiment. On this view the result of our experiment may be summarized by the statement that displacement of the hydrogen by a hot hydrogen atom occurs with complete retention of configuration within the experimental accuracy of 10%.

Discussion

The result that configuration is retained was expected both on the basis of earlier results in related systems and also on the basis of the developing model of these hot reactions.[4,6] Displacement of hydrogen atoms without inversion previously has been demonstrated in the condensed phase for glucose[8] and alanine.[9] In the gas phase, systems such as neopentane had provided similar though less conclusive indications.[6] Were displacement to proceed chiefly by Walden inversion, it might well have been expected that hydrogen displacement in neopentane would have been sterically hindered and that instead, expulsion of methyl to form isobutane should be favored. Nothing of the kind was observed. Similarly the *direct* displacement of hydrogen at an sp^2 carbon atom seems to occur with retention of configuration[6] (although excitation introduced in the process may subsequently cause rotation about the double bond).

All of these findings point to the inductive generalization of the result obtained for the C–H bond at the asymmetric carbon in 2-butanol: hot hydrogen displacement of hydrogen occurs with retention of configuration of all systems. (See however footnote 20 regarding very simple systems.)

The fact that racemization does not occur on displacement is, of course, to be expected if no internally equilibrated metastable intermediate is formed. Beyond this, the fact that configuration is retained rather than inverted is also consistent with the model of a fast, direct reaction occurring in about 10^{-14} sec.—the time required for an H atom in the electron volt range to traverse 1Å. A fast event, caused by a small atom, will be localized—as is evident from the result that 99% of the reaction products can be accounted for by the rupture of one or, much less frequently, two bonds.[6] In such a fast, localized collision it would be difficult to excite the necessary vibrational and rotational modes to effect the relatively ponderous inversion of the three attached groups about the central carbon atom. There is another, related reason why hot hydrogen displacement with inversion is unlikely. In order to capture the incoming tritium atom, the central carbon atom must make an orbital available for it before it rebounds. But the time interval for which the fast rebounding atom is in the vicinity of the carbon is considerably shorter than the time required to effect the inversion and thus make the orbital available.[20] Thus,

(20) In a very simple molecule, particularly methane, the time scale of the inversion of the three light hydrogen atoms could become comparable to that of the collision itself. Thus if the tritium strikes

instead of displacing hydrogen by Walden inversion, the hot hydrogen atom is much more likely to interact with a single bond, ejecting the atom thus bound. In such a displacement an orbital to capture the hot atom becomes available rapidly since the motion of other nuclei in the molecule is not required.

It is interesting to contrast this situation with thermal displacement reactions involving ions. These frequently occur with inversion of configuration. Apparently here the motion of the incoming group is sufficiently slow, and its size sufficiently large, so it can initiate the concerted inversion of the whole system around its center.

The activation energy for hydrogen atom displacement in methane by inversion has been calculated to be 1.6 ev.[21] The fact that this might well be less than the minimum energy for displacement with retention of configuration does not affect the argument. On the one hand the inversion mechanism will be ineffective if, as is believed to be the case here, there is no effective coupling mechanism to put the required energy into the appropriate vibrational modes. On the other hand, ample energy is available for the non-inversion displacement.

This model of hydrogen displacement emphasizes that equilibrium rate theory is clearly inapplicable to such a hot reaction. Nor is there any question of the existence of a common intermediate. There are of course intermediates in the displacement in that there are collision complexes. But there are an infinite number of these collision complexes; there can be no equilibration of energy within them for they do not survive for even one vibration; and the products that arise from each of them have already been predetermined by the manner in which the complex was formed. The connotation of the term "collision complex" is thus quite different from that normally assumed for thermal reactions. In hot processes it merely denotes that stage of the collision in which the participants are closest together.

the carbon atom, inversion with capture of the tritium may be possible. Although from geometrical considerations collision with a single C–H bond to give displacement with retention of configuration still seems much more probable, displacement with inversion may no longer be as unlikely as it is in more complex molecules. Unfortunately an experimental test of this point seems most difficult.

(21) E. Gorin, W. Kauzmann, J. Walter and H. Eyring, J. Chem. Phys., 7, 633 (1939).

The present model of the hot hydrogen displacement reaction may be summarized as: (1) When a hydrogen atom with a kinetic energy of the order of 2–10 ev. strikes a molecule, there is a high probability, approaching one-half,[4] that it will react. The fact that the collision efficiency is so much higher than for most thermal reactions is, of course, in part due to the absence of atoms with less than the activation energy. Even more significant is the fact that the energy of the hot atoms is sufficiently in excess of the activation energy that reaction becomes possible even if the point and direction of impact are energetically unfavorable. In terms of the passage of the system over the reaction energy surface this means that the possible paths are not restricted to those leading over the lowest saddle point. Many kinds of reactive collisions become possible and differences in activation energy no longer determine the path and possible products of reaction. (2) The velocity, small size and high energy of the hot atom lead to a fast, localized displacement occurring in about the characteristic time of one bond vibration. There is insufficient time to transfer energy within the molecule and to excite complex molecular vibration during the time of the initial displacement. For this reason the great majority of reactions involve the rupture of only a single bond with no rearrangement. Similarly it is difficult to excite the concerted, relatively slow vibration of several groups that would lead to an inversion of configuration. (3) The course of the reaction is primarily decided by the angle and point of impact. Abstraction results from approach along the C–bond axis, while displacement occurs when the bond is approached from large angles to this axis. Steric considerations are thus dominant in this "Impact Model." These considerations and the evidence they provide for the model are discussed in the preceding paper.[6]