the procedure described for I hydrochloride, except that the reaction mixture was allowed to stand for five days; yield 242 g. This hydrochloride (123.5 g.) was added slowly to an ice-cold mixture of 500 ml. of water, 276 g. of potassium carbonate and 200 ml. of ether, with rapid stirring. The aqueous layer was extracted once with 100 ml. of ether, and the combined ether solutions were dried over sodium sulfate and distilled through an adiabatic, total reflux, variable take-off type column with a 70 × 1.2 cm. section packed with glass helices. The yield of acetimino ethyl ester was 19.0 g. (22%), b. p. 89.7–90° (765 mm.); $n^{25}D$ 1.4025; d^{25}_4 0.8671; M_D calcd. 24.27, found 24.49.[13]

Summary

The ultraviolet absorption curve (in cyclohexane) of ethyl β-dimethylaminocrotonate (III) has a maximum at 2750 Å. (log ε = 4.33), corresponding to the absorption of the conjugated system present. Ethyl β-aminocrotonate (I) and ethyl β-methylaminocrotonate (II) absorb in the same region with similar intensity, confirming their structure as "enamines." Enamine structures have been assigned to these compounds by von Auwers and Susemihl on the basis of their exaltation in refraction.

Ultraviolet absorption and exaltation in refraction also prove that a conjugated system is present in ethyl β-amino-β-ethoxyacrylate, and accordingly the enamine structure V is assigned to this compound. V is a tautomer of monoiminomalonic ester. Its enamine structure is in contrast to the non-enolic structure of ethyl malonate.

Four compounds, either lactones or esters, related in structure to V (IV, VII, IX and X, ref. 3) have ultraviolet absorption spectra which show that they contain conjugated systems and consequently are enamines rather than isomeric imino compounds.

(13) Brühl, *Z. physik. Chem.*, **22**, 388 (1897); and Kohlrausch, *ibid.*, **B38**, 72 (1937), report similar physical constants.

NEW YORK, N. Y. RECEIVED NOVEMBER 15, 1944

[CONTRIBUTION FROM THE RICHMOND LABORATORIES, CALIFORNIA RESEARCH CORPORATION]

Investigation of the Mechanism of Butane Isomerization Using Radioactive Hydrogen as a Tracer

BY T. M. POWELL[1] AND E. B. REID[2]

With increasing commercial importance of the isomerization of paraffin hydrocarbons, a knowledge of the mechanism of these reactions becomes of greater interest. Several mechanisms have been proposed but many have been without experimental foundation[3,4] and there have been few attempts to apply any specific function to the catalyst. The recent work of Heldman[5,6,7] is an independent work giving many of the conclusions obtained in this paper.

Utilizing the radioactive hydrogen isotope, H^3 (hereafter called tritium, abbreviated as T), as a tracer, an attempt has been made to determine the steps involved in the reaction, *n*-butane ⇆ isobutane, carried out over aluminum chloride on alumina and charcoal supports.

A number of investigations have been made using tritium as a tracer in chemical and hydrogen exchange reactions.[8–12] Advantage is taken in this case of the fact that during catalytic isomerization, an exchange of hydrogen atoms from both elementary hydrogen (H_2) and hydrogen chloride with the hydrogen atoms of butane occurs. The presence of hydrogen apparently does not alter the progress of the reaction, whereas hydrogen chloride is essential as shown by previous investigations.[13]

Materials.—The tritium used in these experiments was furnished through the courtesy of the Radiation Laboratory of the University of California, and was produced by deuteron–deuteron bombardment during operation of the sixty-inch cyclotron at Berkeley. It was obtained in the chemical form of water with a specific activity of 5.0 × 10^9 disintegrations per mole per minute.

The gaseous radioactive hydrogen was prepared by electrolyzing a dilute acid solution of this water in a glass cell fitted with platinum electrode separated by a sintered glass plate to prevent diffusion of the evolved gases.

The normal butane was removed from an industrial gas fraction by successive fractional distillation. The isobutane was prepared from isobutene (made by dehydrating tertiary butyl alcohol over alumina) by hydrogenation with electrolytic hydrogen over a copper catalyst prepared after the manner of Kistiakowsky, *et al.*[14] The normal butane and the isobutane used in the experiments were over 99% pure.

The radioactive hydrogen chloride was prepared by treating the electrolyzed radioactive hydrogen with elementary chlorine over an activated carbon catalyst at 300° and by dropping radioactive sulfuric acid (96%) on sodium chloride.

The butanes with the selectively placed tritium atoms were prepared by hydrolyzing the corresponding butyl magnesium bromides with acid solutions of radioactive

(1) Present address: Standard Oil Company of California, San Francisco, Calif.

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(3) Montgomery, McAteer and Franke "Catalytic Isomerization of Paraffin Hydrocarbons," Petroleum Division, A. C. S. Meeting, Preprint Baltimore Meeting, 1939.

(4) Egloff, Komarewsky and Hulla, "Hydrocarbons and Their Isomerization," same as above.

(5) Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943).

(6) Heldman, *ibid.*, **66**, 1786 (1944).

(7) Heldman, *ibid.*, **66**, 1789 (1944).

(8) Allen and Ruben, *ibid.*, **64**, 948–950 (1942).

(9) Harman, Stewart and Ruben, *ibid.*, **64**, 2293–2294 (1942).

(10) Fontana, *ibid.*, **64**, 2503–2504 (1942).

(11) Norris, Ruben and Allen, *ibid.*, **64**, 3037 (1942).

(12) Harman, Stewart and Ruben, *ibid.*, **64**, 2294–2296 (1942).

(13) Glasebrook, Phillips and Lovell, *ibid.*, **58**, 1944 (1936).

(14) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 65–75 (1935).

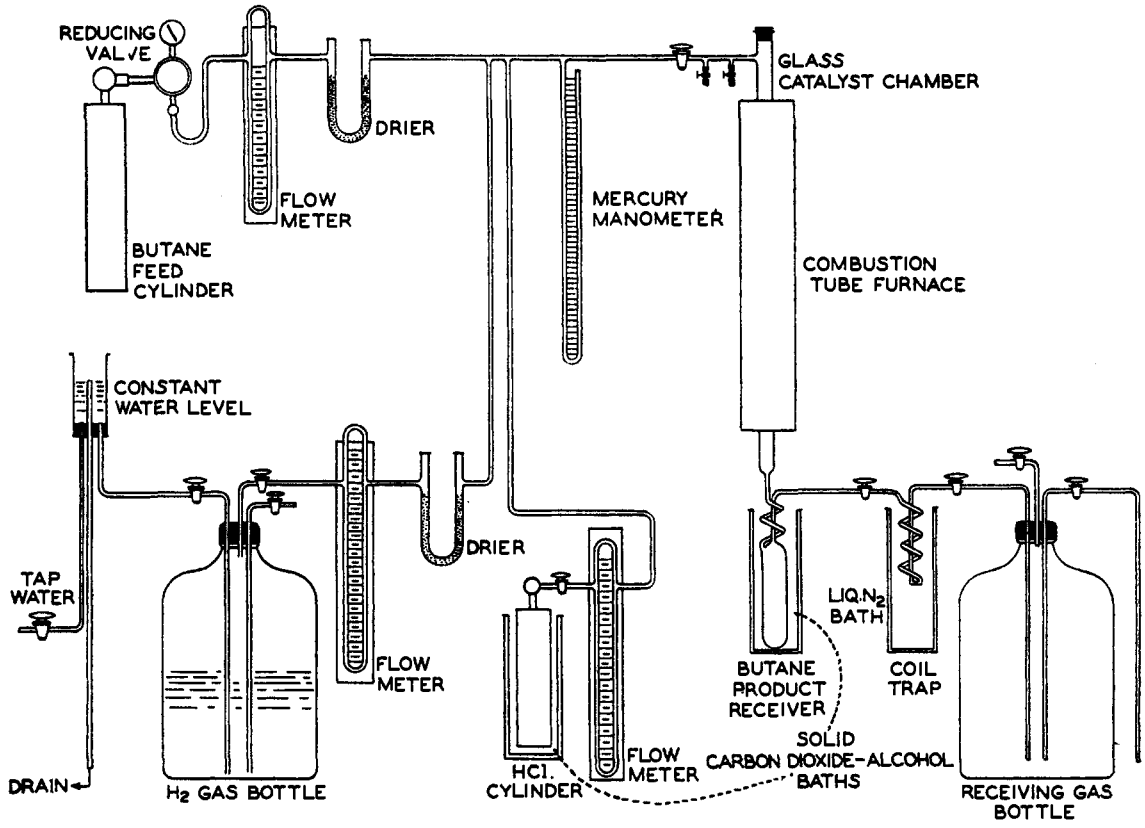


Fig. 1.—Apparatus for butane isomerization-tritium transfer experiments

water. The evolved gases were collected and fractionally distilled. Only the middle fractions thereof were used.

The catalysts were prepared in a hydrogen chloride atmosphere by impregnating the 8–14 mesh supports with aluminum chloride at 316° in a closed system.

Experimental Procedure

All isomerization experiments were carried out at atmospheric pressure with temperatures in the range of 107 to 128°. The flow diagram of the isomerization equipment is shown in Fig. 1. The feed butane, contained in a steel cylinder as a liquid under pressure, was vaporized through a reducing valve and conducted through a flow meter and a drier to a glass catalyst chamber inserted in a combustion tube furnace. In Runs 3, 8, and 22 in Table II, the radioactive hydrogen chloride was dissolved in the butane. In Runs 24 and 25, the hydrogen chloride was contained alone in a steel cylinder as a liquid under pressure at the temperature of a solid carbon dioxide–alcohol bath and was fed into the system as a gas through a needle valve and flow meter. The hydrogen was contained in a gas bottle with water as the displacing liquid. The pressure was held sufficiently above atmospheric to allow throttling through a needle valve for desired rates. The gas was passed through a flow meter, dried and led into the catalyst chamber with the butane. The exit gases were passed through a condenser immersed in a solid carbon dioxide–alcohol bath, a liquid nitrogen coil trap, and to a receiving gas bottle. Sufficient liquid sample was collected for fractional analysis during the course of which middle fractions were removed for tritium analyses.

The tritium analyses were effected as follows: The container of the sample, in a solid carbon dioxide–alcohol bath, was first attached to a high vacuum system. A small portion of the butane was then pumped out to flush out fixed gases, after which the butane gas was admitted to the Geiger–Mueller counter. Because of the weak radiation of the tritium (β-particle range 1 mm. in air), the material to be counted had to be placed inside the counter as the counter gas itself. Fortunately, butane proved to be a good counter gas. Although mixtures of hydrogen and butane may be used as counter gases, the tolerable amount of hydrogen is small. Because of this, the tritium analyses of the hydrogen from exchange experiments with radioactive butanes were made upon butane prepared by hydrogenating butene with the hydrogen to be analyzed. In this hydrogenation procedure, the same copper catalyst was used as in the preparation of the pure isobutane. The counting pressure was usually about 4 cm., which required a counting voltage of 1800 volts. Two sizes of counters were used depending upon the activity of the sample to be counted. They had volumes of 482 cc. and 41.4 cc.

Results and Discussion

The Exchange Reaction, $HT + C_4H_{10} \rightarrow H_2 + C_4H_9T$.—The data are summarized in Table I (Runs 1, 2, 4, 5, 6, 7, 11, 12, 13, 14, 18).

These data show that the isomerized product always had the higher concentration of tritium and that the amount of exchange (for the same catalyst) was roughly proportional to the amount of isomerization occurring. This holds regardless of the charging stock (*i. e.*, normal or isobutane). There is, however, quite a difference in the amount of exchange obtained with the various catalysts, which is most marked between the charcoal and alumina supported groups. The charcoal supported catalysts are characterized by a low exchange activity relative to isomeriza-

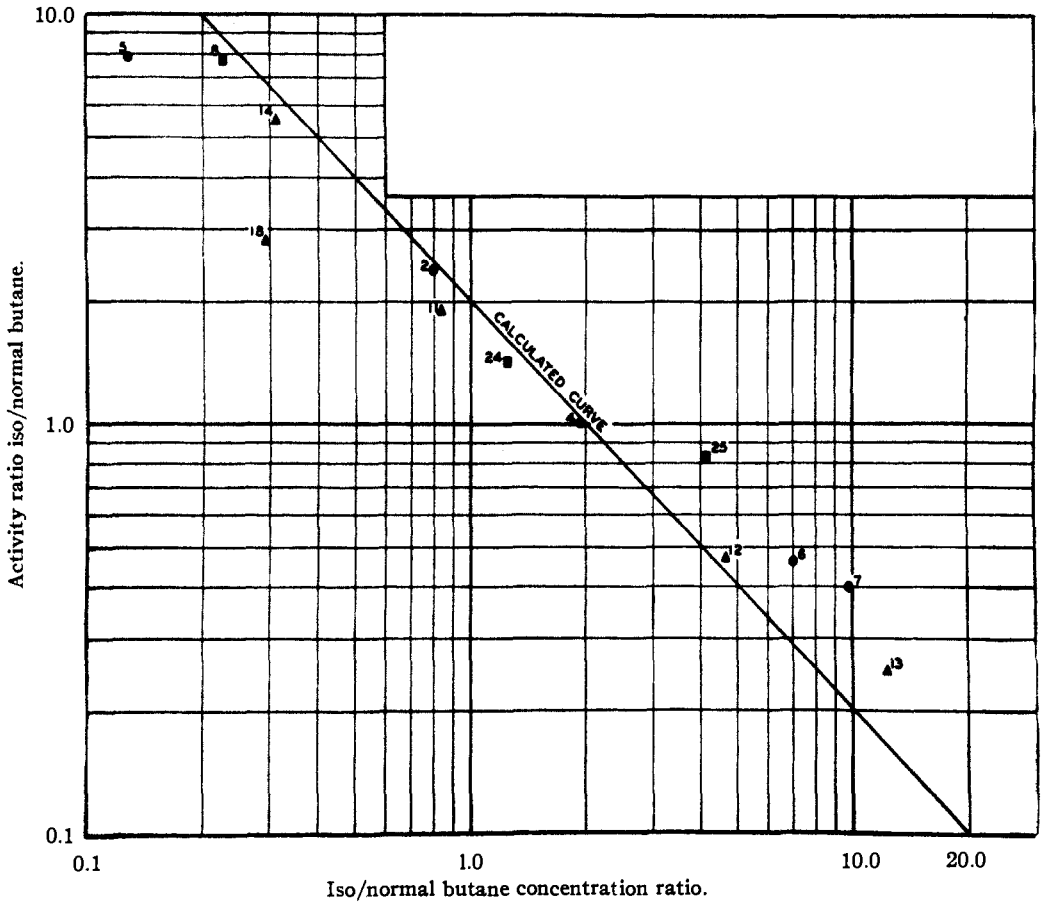


Fig. 2.—Tritium transfer-butane conversion relationship, tritium contained in molecular hydrogen feed: ●, aluminum chloride on charcoal; ▲, aluminum chloride on alumina; tritium contained in hydrogen chloride: ■, aluminum chloride on alumina.

tion although the ratios of exchange to the two isomers are essentially the same for both groups of catalysts.

Attempts to devise a mechanism of the exchange which will explain the ratios of exchange to the two isomers have not been entirely successful. By hypothesizing the existence of a butane–$AlCl_3$ complex, during the life of which exchange occurs with subsequent decomposition of the complex in an equilibrium manner with respect to the iso and normal butane equilibrium, a reasonably satisfactory correlation of the experimental results may be obtained. The results of correlating the data in this manner are shown graphically in Fig. 2 in which the ratios of isobutane to normal butane in the product are plotted against the ratios of tritium content in the isobutane and normal butane. At low conversions there is a definite displacement of the experimental from the calculated values.

The Exchange Reaction, $TCl + C_4H_{10} \rightarrow HCl + C_4H_9T$.—The data are summarized in Table II (Runs 3, 8, 21, 22, 23, 24, 25).

Previous investigators have pointed out that hydrogen chloride is necessary as a promoter in reactions of this sort with aluminum chloride. The large amount of exchange of tritium from radioactive hydrogen chloride to the butanes is further evidence of some integral participation of the hydrogen chloride in the isomerization. As in the case of the hydrogen exchange, the higher concentration of the tritium occurs in the isomerized product. With approximately the same divergence from the calculated values as in the $HT + C_4H_{10} \rightarrow C_4H_9T + H_2$ reaction, the results can be explained on the basis of a complex formation, exchange, and equilibrium decomposition sequence as shown by some of the points in Fig. 2.

In a discussion of the hydrogen chloride exchange, it should be pointed out that the catalysts used in these experiments were prepared under partial pressures of hydrogen chloride and, therefore, contained considerable amounts of hydrogen chloride. If such a catalyst, without further treatment, is used with TCl, there is no observable tritium in the product butanes as shown by the results of Run 22. When this catalyst was heated to 121° and flushed with hydrogen at a rate of 4 gas volumes/volume of catalyst/min. for three hours and then used, the

TABLE I

THE REACTION, $HT + C_4H_{10} \rightarrow H_2 + C_4H_9T$

Run no.	1	2	4	5	6	7	11	12	13	14	18
Catalyst: support and wt. % aluminum chloride	Charcoal[a] 0	40	40	40	40	40	Alumina[a] 20	20	20	20	20
Temperature, °C.	121	121	121	121	121	121	124	123	122	123	124
HCl, gas vol. % of butane feed	1.8	1.8	1.8	1.8	0	0	<0.2	<0.2	<0.2	<0.2	0
HCl activity, counts/mole/min.	0	0	0	0	0	0	0	0	0	0	0
Charging stock	n-C_4	n-C_4	n-C_4	n-C_4	i-C_4	i-C_4	n-C_4	i-C_4	i-C_4	n-C_4	n-C_4
C_4 feed rate, liq. v/v/hr.	0.1	0.1	0.1	0.05	0.05	0.05	0.1	0.1	0.2	0.2	0.1
C_4, counts/mole/min.	0	0	0	0	0	0	0	0	0	0	0
H_2 feed rate, mole/mole C_4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
H_2, counts/mole/min. $\times 10^{-7}$	2.34	2.34	0.8	1.0	1.0	1.0	1.12	0.81	0.81	0.76	0.75
Product analysis											
C_3, vol. %	0	4.1	5.9	0.5	0.9	0.3	0.4	2.0	1.3	0.6	1.0
i-C_4, vol. %	0	40.6	58.7	11.4	85.1	88.1	44.2	78.9	89.2	23.4	22.3
n-C_4, vol. %	100	51.4	30.3	88.1	12.2	9.2	53.0	17.0	7.3	74.5	75.8
C_5+, vol. %	0	3.9	5.1	0	1.8	2.4	2.4	2.1	2.2	1.5	0.9
Tritium analyses											
C_3, c./m./m. $\times 10^{-5}$			4.8								
i-C_4, c./m./m. $\times 10^{-5}$		3.30	3.77	1.56	0.23	0.16	7.24	2.53	1.09	1.84	6.65
n-C_4, c./m./m. $\times 10^{-5}$	0	1.39	3.77	0.21	0.50	0.40	3.84	5.37	4.42	0.34	2.39
Iso/normal, vol. ratio		0.80	1.94	0.13	7.0	9.8	0.84	4.65	12.32	0.314	0.295
Iso/normal, act. ratio		2.37	1.0	7.8	0.46	0.40	1.88	0.470	0.247	5.50	2.78
% Act. in i-C_4[b]		0.57	2.77	0.18	.19	.14	2.85	2.46	1.20	0.57	1.98
% Act. in n-C_4		.30	1.43	.19	.06	.04	1.82	1.13	0.40	.33	2.42
% Act. in C_4 (total)		.87	4.20	.37	.25	.18	4.67	3.59	1.60	.90	4.40

[a] Charcoal was Columbia Activated Carbon, 8–14 mesh. Alumina was Alorco 'Grade A' activated alumina, 8–14 mesh.
[b] Per cent. of original activity in hydrogen appearing in these hydrocarbon fractions.

TABLE II

THE REACTION, $TCl + C_4H_{10} \rightarrow HCl + C_4H_9T$

Run no.	3	8	21	22	23	24	25
Catalyst support wt. % aluminum chloride	Charcoal 40	Alumina 20	Alumina 20	Alumina 20	Alumina 20	Alumina 20	Alumina 20
Temperature, °C.	121	121	107	107	121	121	121
HCl, gas vol. % of butane feed	2.5	2.5	0	20	0	20	10
HCl activity, counts/mole/min. $\times 10^7$	0.97	0.97	0	0.97	0	15.7	15.7
Charging stock	n-C_4	n-C_4	n-C_4	n-C_4	n-C_4	n-C_4	i-C_4
C_4 feed rate, liq. v./v./hr.	0.2	0.1	0.1	0.2	0.1	0.1	0.2
C_4, counts/mole/min.	0	0	0	0	0	0	0
H_2 feed rate, mole/mole C_4	0	1.0	1.0	1.0	1.0	1.0	1.0
H_2, counts/mole/min.	0	0	0	0	0	0	0
Product analysis							
C_3, vol. %	0.5	0	1.5	0.1	1.1	1.4	2.1
i-C_4, vol. %	5.3	18.5	48.9	45.3	34.0	53.4	76.0
n-C_4, vol. %	94.2	81.5	48.1	53.5	64.9	42.5	18.3
C_5+, vol. %	0	0	1.5	1.1	0	2.7	3.6
Tritium analyses							
i-C_4, c./m./m. $\times 10^{-5}$	1.36	1.29		0[b]		0.69	0.23
n-C_4, c./m./m. $\times 10^{-5}$	0?	0.18		0[b]		.49	.27
H_2, c./m./m.		0?		0		0	0
Iso/normal, vol. ratio	0.055	0.228	1.01	0.85	0.53	1.26	4.15
Iso/normal, act. ratio	∞?	7.7				1.41	0.83
% Act. in i-C_4[a]	2.90	10.0	[c]		[c]	11.7	10.9
% Act. in n-C_4		5.6				6.7	3.2
% Act. in C_4 (total)		15.6				18.4	14.1
% Act. in H_2		0				0	0

[a] Per cent. of original activity in hydrogen chloride appearing in these hydrocarbon fractions. [b] Lack of exchange to butanes attributed to fact that catalyst contained large amount of inactive hydrogen chloride from preparation. [c] Catalyst activity checks.

large amounts of exchange shown in Runs 24 and 25 were obtained. This necessity of removing the non-radioactive hydrogen chloride before observing the hydrogen exchange appears explicable on the basis of the formation of the compound $HAlCl_4$ which is probably the catalytic substance and has a low decomposition pressure. There is, however, no direct evidence of such a

TABLE III

THE REACTION, $C_4H_9T + H_2 \rightarrow HT + C_4H_{10}$

Run no.	9	10	15	16	17	19	20
Catalyst support	Alumina	Alumina	Alumina	Alumina	Alumina	Alumina	Alumina
wt. % aluminum chloride	20	20	20	20	20	20	20
Temperature, °C.	124	121	124	128	121	122	124
HCl, gas vol. % of butane feed	0	0	0	0	0	0	0
HCl activity, counts/mole/min.	0	0	0	0	0	0	0
Position of tritium	Primary	Primary	Secondary	Primary	Tertiary	Tertiary	Primary
Charging stock	n-C_4	n-C_4	n-C_4	i-C_4	i-C_4	i-C_4	i-C_4
C_4 feed rate, liq. v./v./hr.	0.05	0.1	0.1	0.1	0.1	0.1	0.1
C_4, counts/mole/min. $\times 10^{-7}$	3.56	3.56	3.87	3.63	12	12	3.63
H_2 feed rate, mole/mole C_4	1.0	1.0	1.0	1.0	1.0	1.0	1.0
H_2, counts/mole/min.	0	0	0	0	0	0	0
Product analysis							
C_3, vol. %	0	0.5	0.4	1.5	2.3	1.9	1.0
i-C_4, vol. %	15.3	38.0	33.5	85.1	89.2	88.3	82.8
n-C_4, vol. %	84.2	61.5	64.1	8.8	3.7	7.9	11.9
C_5+, vol. %	0.5	0	2.1	4.6	4.8	1.9	4.3
Tritium analyses							
H_2, c./m./m. $\times 10^{-5}$	0	0.15	0.51	3.43	1.52	0.79	1.10
Iso/normal, vol. ratio	0.182	.603	.522	9.70	24.0	11.2	6.96
Iso/normal, act. ratio							
% act. in H_2[a]	0	.043	.132	0.95	0.127	0.066	0.30

[a] Per cent. of original activity in butane appearing in the product hydrogen.

compound given in the literature, although its existence as the catalytic substance in similar reactions has been suggested.[15]

After obtaining these results with TCl, it appeared possible that the observed exchange from the hydrogen to the butanes might go through the sequence

$$HT + HCl \longrightarrow H_2 + TCl$$
$$TCl + C_4H_{10} \longrightarrow HCl + C_4H_9T$$

with no direct exchange between H_2 and C_4H_{10}. To check this, the hydrogen from Runs 8, 24, and 25 was analyzed. The analysis showed no tritium present after reaction. This failure to find tritium in the hydrogen excludes this mechanism of exchange from the hydrogen.

The Exchange Reaction, $C_4H_9T + H_2 \rightarrow HT + C_4H_{10}$.—The data are summarized in Table III (Runs 9, 10, 15, 16, 17, 19, 20).

It might be expected that the amount of exchange of tritium from the butane to the hydrogen could readily be calculated from the previously observed hydrogen to butane exchange, taking into account only the number of participating hydrogens of the butane. This was found, however, not to be true. When the tritium is placed on either the terminal or secondary carbon atoms of the normal butane, the exchange observed is much less than would be predicted from the $HT + C_4H_{10}$ data. The results of Runs 10 and 15 indicate that the hydrogens on the secondary carbons are those which participate principally in this exchange.

(15) Egloff, Wilson, Hulla and Van Arsdell, *Chem. Rev.*, **20**, 345–411 (1937).

The rate or amount of exchange of tritium from a primary carbon of isobutane is greater than from a tertiary carbon atom. With the tritium selectively placed on the primary carbon atom in isobutane, a more rapid exchange is obtained for the reaction, $C_4H_9T + H_2 \rightarrow C_4H_{10} + HT$, than in the reverse reaction, $C_4H_{10} + HT \rightarrow C_4H_9T + H_2$. This conclusion allows for the number of participating hydrogens in the isobutane. That the exchange should occur at different rates, depending upon in which substance the tritium is originally present, is a rather startling result. Such an anomalous effect is unexplained at present, excluding possibly, the unique chemistry of tritium, about which there is little available knowledge at present.

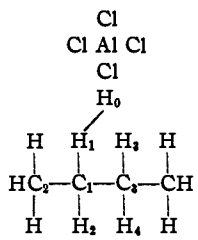
Proposed Mechanism.—The exchange of hydrogen atoms between butane and molecular hydrogen offers little information usable in interpreting the mechanism of isomerization except that somewhere in the process, the molecule becomes vulnerable to attack by hydrogen, while the large amounts of exchange with hydrogen chloride point toward a more integral participation by it in the reaction. The following proposed mechanism is compatible with these ideas.

In proposing this mechanism some assumptions which are as yet lacking experimental verification are made, namely: 1. That in the presence of hydrogen chloride and a suitable support aluminum chloride forms the compound $HAlCl_4$. This is supported by the fact that aluminum chloride forms numerous addition compounds of the type

$AlCl_3NaCl$.[16] 2. That in this state of combination, the $AlCl_4$ portion of the molecule (having a stabilizing spherical symmetry) gives rise to a weakening of the H—Cl bond. 3. That the hydrogen is oriented outward from the catalyst surface such that contact between the butane and the catalyst be made in a manner that this hydrogen enters into the bonding spheres of the carbon atoms of the butane molecule.

Equipped with the preceding assumptions, the following steps are proposed as those occurring in the reaction, n-$C_4H_{10} \rightarrow$ iso-C_4H_{10}:

1. The butane contacts the catalyst mass such that the hydrogen of the hydrogen chloride in combination with $AlCl_3$ (designated as H_0 in the diagram) enters the bonding sphere of the carbon atom (designated as C_1) of the butane.



2. A weakening of the bond between C_1 and C_2 with a partial rupture occurs because of the presence of 3 hydrogen atoms and 2 carbons about the same bonding volume of C_1. This particular C—C bond is believed to be affected most as the Et–Et linkage is symmetrical and hardly susceptible to this type of rupture.[3]

3. At this point, the $AlCl_4$ exists essentially minus its hydrogen in a position intermediate between C_1 and C_3. In such a position, there is a tendency to acquire a hydrogen from C_3 thus leaving a situation of unfilled bond position distributed between C_1 and C_3 so that the methyl group C_2 may either become bonded with C_3 to form isobutane or reattach itself to C_1 to return to the original normal butane form.

The reverse reaction, isobutane $\rightarrow$ normal butane, can be readily explained by the same steps in reverse order. The butane makes contact with the catalyst so that the catalyst hydrogen enters the bonding sphere of the tertiary carbon, bringing about a weakening and rupture of one of the C—C bonds. At this point, the state of the system is the same as Step 3 in the forward reaction. It is, therefore, purely a matter of thermodynamic stability whether the iso or the normal compound will be formed.

The hydrogen exchange from the hydrogen chloride as shown in this mechanism would be large, the tritium originally present in the HCl going into the butanes. This is observed in the experiments. The exchange of tritium from hydrogen to the butane would be expected to be smaller in amount than from the HCl, which is also verified by the data. It is likely that this exchange from the hydrogen takes place at that point represented at the beginning of forward step No. 3. This situation is favorable for exchange in that the bond is partially olefinic and hydrogens adjacent to double bonds have been shown[17] to be available for such exchanges with hydrogen; also the hydrogen is displaced in some degree from a normal bonding position and thus presents some likelihood of entering the bonding sphere of an adjacent hydrogen molecule. This, as an approximation, may be likened to the exchange observed between atomic hydrogen and hydrogen.

Pauling[16] has pointed out that crystal studies of compounds of the type AlX_3 show that each halogen is contained between two aluminum atoms and that there is a bond between the atoms in the crystal requiring each crystal to be regarded as a sort of giant polymer. This process of fusion involves the breaking of these chemical bonds between a metal and a non-metal as also does the formation of $HAlCl_4$ from the crystalline aluminum chloride and hydrogen chloride. It would, therefore, be expected that the aluminum halide with the lowest melting point would add the corresponding hydrogen halide with the least difficulty and that if the compound $HAlX_4$ is the catalytic material, melting point of the aluminum halide would be an index of isomerization activity.

Comparing the melting points of the aluminum halide we find AlF_3, 1040°, $AlCl_3$, 194°, $AlBr_3$, 97.5°. The activities correlate well, increasing in order of decreasing melting points, AlF_3 shows no activity at all, while both $AlCl_3$ and $AlBr_3$ are active, with $AlBr_3$ the more active of the two.

Paraffin and olefin isomerization have in common the one operation of shifting a hydrogen atom. In paraffin isomerization there must occur in addition some alkyl shift, whereas some simpler types of olefin isomerization involve only the single hydrogen shift. Isomerizations of this type are characterized by the ease with which they take place. In reviewing the type of catalysts that effect this reaction at low temperatures, it is found that they consist of substances that have large central groups from which a hydrogen protrudes. Examples are phosphoric acid, perchloric acid, and benzenesulfonic acid.

In summation of the preceding discussion, it is believed that catalysis of hydrocarbon isomerization is that process of providing an hydrogen atom for the entering of the bonding sphere of a carbon atom thus displacing a methyl group (or hydrogen) from its normal position by a mechanism involving the inversion of a carbon bond (comparable to the Walden inversion), but at the same time keeping the methyl group in the system, catalyst plus hydrocarbon, in a manner that, upon the breaking up of this system, the methyl group will reattach itself to the molecule in a position deter-

(16) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(17) Morikawa, Trenner and Taylor, THIS JOURNAL, 59, 1103-1111 (1937).

mined by the thermodynamic stability of the various isomers.

Summary

1. The results of tritium exchange between hydrogen, hydrogen chloride, and butanes during isomerization are presented. These show that exchange of tritium in hydrogen chloride to butane is large compared to exchange of tritium in hydrogen (HT) to butane.

2. A mechanism is proposed which qualitatively explains the data.

3. A general mechanism of hydrocarbon isomerization is presented.

RICHMOND, CALIFORNIA RECEIVED DECEMBER 13, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The First Ionization of Carbonic Acid in Aqueous Solutions of Sodium Chloride

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From the electromotive forces of the cells without liquid junction

$$\text{Pt-H}_2,\ CO_2\,|\,NaHCO_3(m_1),\ NaCl(m_3),\ CO_2(m_2)\,|\,AgCl\text{-}Ag$$

Harned and Davis[2] determined the first ionization constant of carbonic acid in water. They also showed that this cell may be used to determine the ionization, $m_H m_{HCO_3}/m_{CO_2}$, in salt solutions if the solubility of carbonic dioxide in these solutions is known and, as a contribution to this objective, they measured m_{CO_2} in sodium chloride solutions at concentrations up to 3 M and throughout the temperature range 0 to 50°.

We have now extended these cell measurements in a manner suitable for the determination of the ionization in sodium chloride solutions up to a concentration of 1 M salt and at temperatures from 0 to 50°. From these ionization data, the heat content, specific heat and entropy of ionization have been computed over the above ranges of concentration and temperature.

A very careful analysis of the equilibrium data has been made and equations constructed by which the ionization constant, $K_{(S=0)}$, the ionization, $K_{(S)}$, the molalities, m_H and m_{CO_2}, and the activity coefficients, $\gamma_H\gamma_{HCO_3}/\gamma_{CO_2}$ may be calculated with a high order of accuracy.

General Method of Procedure

The equation for the electromotive force, E, of the cell is

$$E = E^0 - \frac{RT}{F}\ln m_H m_{Cl}\gamma_H\gamma_{Cl} + \frac{RT}{2F}\ln P_{H_2}$$
$$= E^0 - E_c - \frac{RT}{F}\ln m_H m_{Cl}\gamma_H\gamma_{Cl} \qquad (1)$$

where E^0 is the standard potential at one atmosphere hydrogen pressure, E_c equals $(-RT/2F)$ ln P_{H_2} and the other symbols have their usual significance.[3] The dissociation equilibrium under consideration is given by

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

and the ionization constant is defined by

$$K_{(S=0)} \equiv \frac{a_H a_{HCO_3}}{a_{CO_2}a_{H_2O}} = \frac{\gamma_H\gamma_{HCO_3}m_H m_{HCO_3}}{\gamma_{CO_2}a_{H_2O}m_{CO_2}} = \frac{\gamma_H\gamma_{HCO_3}}{\gamma_{CO_2}a_{H_2O}}K_{(S)} \qquad (3)$$

As a reference state, we choose the condition that $\gamma_H = \gamma_{HCO_3} = \gamma_{CO_2} = a_{H_2O} = 1$ in pure water at every temperature, and therefore $K_{(S=0)}$ becomes an isothermal constant at all salt concentrations.

By elimination of m_H from equations (1) and (3), the expression used by Harned and Davis for the determination of $K_{(S=0)}$

$$-\log K' = -[\log K_{(S=0)}] + \log\frac{\gamma_H\gamma_{Cl}a_{H_2O}\gamma_{CO_2}}{\gamma_H\gamma_{HCO_3}} =$$
$$(E + E_c - E^0)\frac{F}{2.303RT} + \log m_{CO_2} + \log\frac{m_{Cl}}{m_{HCO_3}} \qquad (4)$$

is obtained. Since the logarithmic term containing the activity coefficients becomes unity in pure water, $[-\log K_{(S=0)}]$ may be obtained by extrapolating the right side of this equation to zero concentrations of all solutes. This requires a double extrapolation, firstly to zero concentration of electrolytes and finally to zero concentration of carbon dioxide. Harned and Davis, by employing gas mixtures containing from 18 to 80% carbon dioxide showed that the presence of carbon dioxide had no appreciable effect upon $[-\log K']$. This important fact eliminates the necessity of the double extrapolation and greatly reduces the number of measurements required.

By elimination of log $K_{(S=0)}$ from equations (3) and (4), we obtain

$$-\log\frac{m_H m_{HCO_3}}{m_{CO_2}} = (E - E^0 + E_c)\frac{F}{2.303RT} +$$
$$\log\frac{m_{CO_2}m_{Cl}}{m_{HCO_3}} + \log\gamma_H\gamma_{Cl} \qquad (5)$$

an expression which may be used to evaluate the ionization, $m_H m_{HCO_3}/m_{CO_2}$, henceforth denoted by $K_{(S)}$, in the salt solutions. We note that this evaluation of $K_{(S)}$ does not require a knowledge of $K_{(S=0)}$. If the activity coefficient function, $\gamma_H\gamma_{HCO_3}/\gamma_{CO_2}a_{H_2O}$, is required, it is apparent from equation (3) that a knowledge of $K_{(S=0)}$ is necessary.

To evaluate $[-\log K_{(S)}]$ at a given sodium

(1) This communication contains material from a dissertation presented by Francis T. Bonner to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

(2) Harned and Davis, THIS JOURNAL, 65, 2030 (1943).

(3) For a thorough discussion of this method as applied to other equilibria involving hydrogen ion, see Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," chapter 15, Reinhold Publishing Corporation, New York, N. Y., 1943.