Alumina: Catalyst and Support. III.[1a]   The Kinetics and Mechanisms of Olefin Isomerization[1b]

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Received September 14, 1959

It has recently been shown by us that certain aluminas have inherent acidic properties. The present study deals with the kinetics of isomerization of 3,3-dimethylbutene (I) and of isomeric *n*-butenes over such aluminas. The isomerization of I was performed at 350° and at various flow rates. At the shortest contact time the main products were isomeric 2,3-dimethylbutenes and a small amount of 2-methylpentenes. At higher contact times 3-methylpentenes and hexenes were also formed. The rate constants for some of these reactions were determined. The relative ease of skeletal rearrangement was found to depend on the rate of formation of carbonium ions and on the stability of the corresponding olefins. The relative rates of isomerization of 1-, *cis*-2- and *trans*-2-butene over alumina were determined. The reaction was found to be stereoselective and the less stable *cis* isomer was formed faster than the *trans* isomer. A similar stereoselectivity occurred when liquid phosphoric acid was used as a catalyst. The mechanism of stereoselective isomerization was discussed; the relative rates of formation of the olefins is governed by the basicities of the corresponding olefins.

In a recent paper[3] evidence has been presented indicating that the catalytic activities of alumina catalysts are a consequence of the acidic properties inherent in activated alumina. This conclusion was based on the fact that alumina-catalyzed reactions are those which are also catalyzed by mineral acids. Furthermore, for catalysts prepared from the same source, there exists a parallelism between the catalytic activity for alcohol dehydration and olefin isomerization on the one hand, and certain indices of surface acidity such as chemisorption of trimethylamine or hydride abstraction from suitable triphenylmethane derivatives on the other hand. Sodium and potassium ions as well as adsorbed ammonia deactivate the alumina catalysts for olefin isomerization.

Additional support for the acid-type activity of alumina is presented in this paper based on a kinetic analysis of the isomerization of 3,3-dimethyl-1-butene (I).

$$\begin{array}{c} \mathrm{C} \\ | \\ \mathrm{C-C-C=C} \\ | \\ \mathrm{C} \qquad \mathrm{I} \end{array}$$
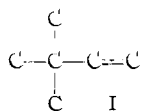
Previous workers[4] had failed to obtain any reaction of I over alumina at 350°, in agreement with the widespread belief that alumina is inactive for reactions involving a change in the carbon skeleton.[5,6]

It was recently shown, however, that over a variety of different alumina catalysts I is skeletally isomerized to a complex mixture of olefins containing up to eleven hexene isomers.[3]

We have now attempted to elucidate the course of the reaction leading to the formation of the different compounds and to substantiate our previously expressed view[3] that olefin isomerization over alumina proceeds *via* carbonium ion intermediates.

While the isomerization of 3,3-dimethyl-1-butene proved to be a useful model reaction for studying the skeletal rearrangement of olefins, the system was too complex for an investigation of the double bond migration in olefins. In spite of the numerous publications dealing with acid-catalyzed olefin isomerization, no information seems to be available in the literature regarding the relative rates of *cis–trans* interconversion *versus* double bond migration.[7a] Furthermore, the detailed stereochemical course of the acid-catalyzed double bond isomerization has not yet received any attention.[7b] Yet such information is of great importance for any mechanism which can be advanced for the isomerization reaction. The *n*-butenes were selected for an investigation of these problems.

In previous investigations[8–12] it was found that the three *n*-butenes are readily interconverted in the presence of mineral acids and metal oxides, yielding an equilibrium mixture. In a kinetic study of the double bond shift in *n*-butenes over alumina, Hay, Coull and Emmett[12] showed that the reaction is reversible and of apparent first order in both directions with the surface reaction and not diffusion as the rate-determining step. The authors made the assumption that the rate constants for the conversion of *cis*-2-butene and *trans*-2-butene to 1-butene are identical. In a similar comprehensive investigation of the isomerization of butene by Turkevich and Smith,[11] it was likewise assumed that whenever there was a shift of the double bond from the 1- to the 2-position, the resulting 2-butene was an equilibrium mixture of the *cis* and *trans* isomers. However, Voge and May[10] in

(1) (a) Presented in part before the Division of Petroleum Chemistry at the Symposium on "Isomerization and Related Processes," American Chemical Society Meeting, April 5–10, 1959, Boston, Mass. (b) For Paper II of this series see H. Pines and G. Benoy, This Journal, **82**, 2483 (1960).

(2) Predoctoral Fellow Universal Oil Products Co. 1956–1957; Tuni Company, Chicago, 1957–1958.

(3) H. Pines and W. O. Haag, This Journal, **82**, 2471 (1960).

(4) P. L. Cramer and A. L. Glasebrook, *ibid.*, **61**, 230 (1939).

(5) K. V. Topchieva, K. Yun-P'n and I. V. Smirnova, in "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 799.

(6) H. N. Dunning, *Ind. Eng. Chem.*, **45**, 551 (1953).

(7) (a) P. J. Lucchesi, D. L. Baeder and J. P. Longwell, This Journal, **81**, 3235 (1959), reported the stereoselective isomerization of 1-butene to *cis*- and *trans*-2-butene. (b) The stereochemistry and kinetics of the carbanion-catalyzed double bond isomerization of olefins has recently been investigated; W. O. Haag and H. Pines, *ibid.*, **82**, 387 (1960).

(8) V. N. Ipatieff, H. Pines and R. E. Schaad, *ibid.*, **56**, 2696 (1934).

(9) W. W. McCarthy and J. Turkevich, *J. Chem. Phys.*, **12**, 405 (1944).

(10) H. H. Voge and N. C. May, This Journal, **68**, 550 (1946).

(11) J. Turkevich and R. V. Smith, *J. Chem. Phys.*, **16**, 466 (1948).

(12) R. G. Hay, J. Coull and P. H. Emmett, *Ind. Eng. Chem.*, **41**, 2809 (1949).

their study on the equilibrium composition of the three n-butenes mentioned unpublished experiments which indicated that starting with 1-butene the cis and trans equilibrium was approached from the cis side. Similarly, 1-butene was recently reported to form preferentially cis-2-butene over alumina[12a] and silica-alumina.[7a]

The three component system consisting of 1-, cis-2- and trans-2-butene was investigated kinetically and the six relative rate constants determined using alumina as a catalyst. A few experiments were also made with liquid phosphoric acid in order to establish whether or not the results obtained with alumina were due to the presence of a solid surface.

Experimental

3,3-Dimethyl-1-butene was prepared from 3,3-dimethyl-butanol[13] according to the published procedure[3]; b.p. 41.0–41.4° (750 mm.), $n^{20}D$ 1.3759 (lit.[14] b.p. 41.14° at 757 mm., $n^{20}D$ 1.3762). The three n-butenes were Phillips Research Grade. The alumina catalyst was prepared by hydrolysis of purified aluminum hydroxide and calcination for four hours at 700° in air. It contained less than 0.001% of sodium and consisted essentially of η-alumina.[3] The catalyst was used in $^1/_8$ inch pellets and in the form of powder passing through 100-mesh screen.

The catalytic reactions were carried out in a Pyrex glass flow reactor and the products were analyzed by gas chromatography. The isomerization of 1-butene by liquid phosphoric acid was achieved by bubbling the reactant gas through the acid by means of a fritted disk.

Results and Discussion

Isomerization of 3,3-Dimethyl-1-butene.—The isomerization of 3,3-dimethyl-1-butene (I) over alumina was performed at 350° and at three different flow rates with the results shown in Table I.

TABLE I

HEXENE ISOMERS OBTAINED FROM THE ISOMERIZATION OF 3,3-DIMETHYL-1-BUTENE OVER ALUMINA[a]

Expt. HLSV[b] Compound	1 6.0	2[d] 2.0	3 0.5	Equil.[c]
3,3-Dimethyl-1-butene	21.0	2.7	1.9	0.5
2,3-Dimethylbutenes	73.0	39.3	23.0	11.5
2-Methylpentenes	6.0	37.2	42.6	40.5
3-Methylpentenes	..	19.8	31.0	33.5
n-Hexenes	..	1.0	1.5	14.1

[a] Temp. 350°. [b] Hourly liquid space velocity = volume of liquid feed per volume of catalyst per hour. [c] Calculated from the published data[15] by linear interpolation. [d] In addition to the hexene isomers, expt. 2 produced 2% of lower boiling material consisting of 2-methyl-2-butene (1%), isobutylene (0.8%) and isobutane (0.2%); expt. 3 also yielded low boiling compounds.

At the highest flow rate (short contact time, expt. 1) the main reaction product is 2,3-dimethyl-butene (II) (a mixture of two isomers). In addition, 6% of 2-methylpentene (III) is formed; it represents a mixture of all the isomers with the 2-methylpentane skeleton and therefore includes 4-methyl-2-pentene. The isomer distribution is compared with the thermodynamic equilibrium values in Table II.

(12a) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(13) V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **73**, 553 (1951).

(14) D. L. Cam'n and F. D. Rossini, *J. Phys. Chem.*, **60**, 1446 (1956).

(15) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. E. Rossini, *J. Res. Natl. Bur. Standards*, **36**, 559 (1946).

TABLE II

ISOMER DISTRIBUTION OF 2-METHYLPENTENES (%)

Isomer	Found[a]	Equil.[b]
C | C=CCCC	1.8	1.9
C | CC=CCC	3.4	2.9
C | CCC=CC	0.8	1.1
C | CCCC=C	0	0.1

[a] Expt. 1. [b] From the published data,[15] normalized to 6%.

It appears that the 2-methylpentenes are present almost in their relative equilibrium concentrations. At the same time, no 3-methylpentene (IV) was detectable. At lower space velocities, however, IV is formed in increasing amounts, until at HLSV = 0.5 III and IV are nearly equilibrated (Table III).

TABLE III

RELATIVE AMOUNTS OF 2- AND 3-METHYLPENTENES PRODUCED, %[a]

Expt. HLSV	1 6.0	2 2.0	3 0.5	Equil.[15]
2-Methylpentenes	100	65.2	57.9	54.8
3-Methylpentenes	0	34.8	42.1	45.2

[a] Normalized to 100.

Only a small amount of n-hexenes is formed. The data in Table I are plotted in Fig. 1 against the reciprocal space velocity as the time variable. From the shape of the concentration–time curves
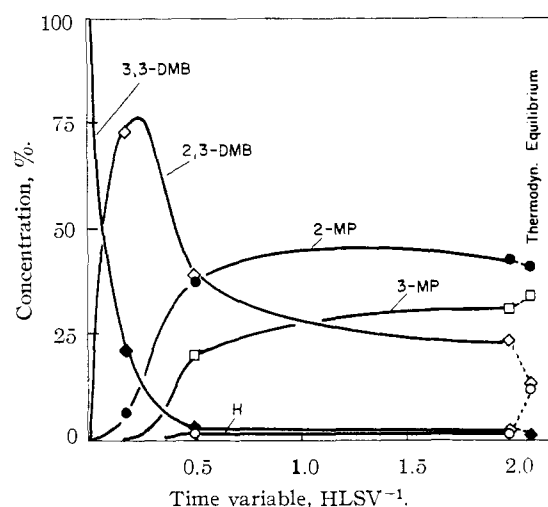

Fig. 1.—Isomerization of 3,3-dimethyl-1-butene; product distribution as a function of the time variable.

it becomes apparent that one deals with consecutive reactions,[16] 2,3-dimethylbutene (II) and 2-methylpentene (III) being the first and second intermediates, respectively. Compound II appears to be the only primary isomerization product. This view is confirmed in Fig. 2, where the relative

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.
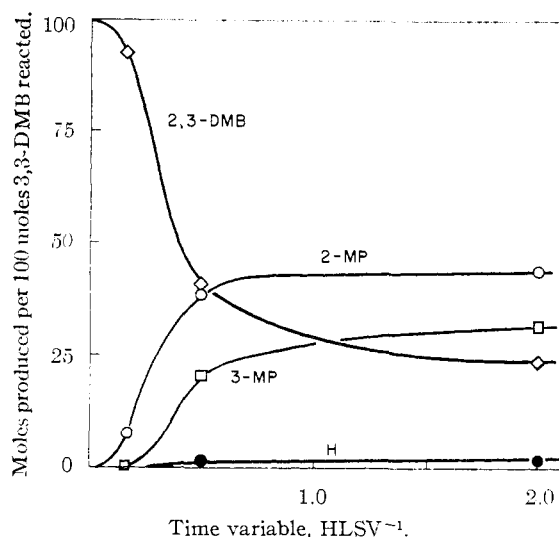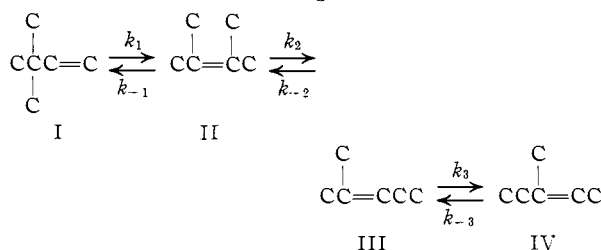
Fig. 2.—Isomerization of 3,3-dimethyl-1-butene: distribution of reaction products vs. time variable.

Fig. 3.—2,3-Dimethylbutenes formed vs. 3,3-dimethylbutene reacted.

concentrations of rearranged olefins (free of unreacted starting material) are plotted against reciprocal space velocity. The extrapolation to zero contact time leads to a value of 100% II.

It also becomes apparent from Fig. 2 that 2-methylpentene (III) and 3-methylpentene (IV) are not formed in parallel reactions, but that at low conversion II is exclusively converted to III.

The isomerization of I over alumina, therefore, is a series reaction following the scheme

$$CCC=C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CC=CC \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}}$$

I   II

$$CC=CCC \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CCC=CC$$

III   IV

For simplicity, only one of the possible isomers is shown for each skeletal structure, while under the experimental conditions used all the double bond isomers are formed in their relative equilibrium concentrations. The small amount of n-hexene formed does not permit us to draw any conclusions as to its precursor. It is assumed, however, that it is formed from 2-methylpentene on mechanistical grounds. The data in Fig. 1 are not in disagreement with this view.

An approximate value of the ratio of rate constants $k_2/k_1 = \kappa$ was obtained by neglecting the reverse reactions k_{-1} and k_{-2}. It is assumed that the reactions follow first-order kinetics, as has been shown to be the case for the isomerization of butenes over alumina.[12] In Fig. 3, the mole fraction of the intermediate II is plotted against the mole fraction of I reacted. Using the relationship[16]

$$\beta_{max} = \kappa^{\kappa/1-\kappa} \tag{1}$$

where β_{max} = experimentally determined mole fraction of the intermediate at the maximum (Fig. 3) and $\kappa = k_2/k_1$, the value of κ was found from a
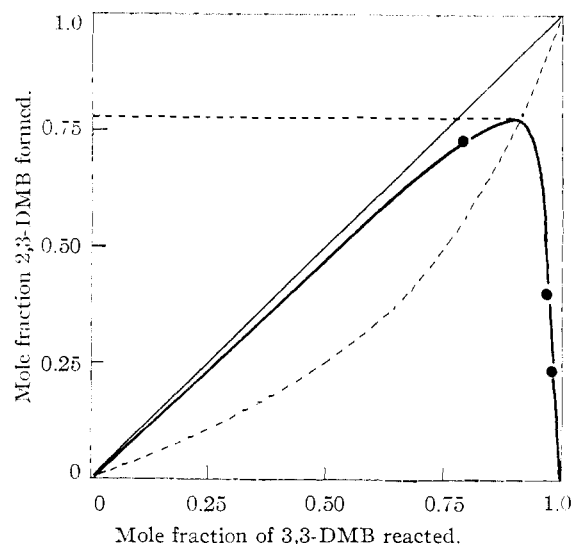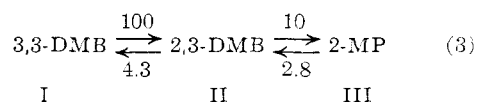
graphical plot of equation 1. For $\beta_{max} = 0.78$ (Fig. 3), $\kappa = 0.10$; thus $k_1/k_2 = 10$.

For a reversible reaction $I \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} II$, the rate constant for the reverse reaction can be calculated from that of the forward reaction by the expression

$$k_{-1} = k_1 (I_e/II_e) \tag{2}$$

where I_e and II_e are the concentrations of I and II at equilibrium. Using this equation and the known[15] relative equilibrium values, the following relative rate constants are calculated

$$3,3\text{-DMB} \underset{4.3}{\overset{100}{\rightleftarrows}} 2,3\text{-DMB} \underset{2.8}{\overset{10}{\rightleftarrows}} 2\text{-MP} \tag{3}$$

I   II   III

Several conclusions can be drawn from the above results which all support the supposition that the skeletal isomerization of 3,3-dimethyl-1-butene over alumina proceeds by a carbonium ion mechanism.

The fact that the 2-methylpentenes were nearly equilibrated before any noticeable amount of 3-methylpentene was formed is in agreement with the general observation that hydrogen migration (to produce double bond isomers) is faster than migration of alkyl groups in reactions believed to proceed through carbonium ion intermediates. For instance, Cannell and Taft[17] found that hydrogen migration is favored over methyl migration by factors of 25 and 5 in n-propyl and isobutyl carbonium ions, respectively.

The formation of small amounts of 2-methyl-2-butene, isobutane and isobutylene is indicative of an acid-catalyzed dimerization of the hexenes[18] and similar olefins[19,20] followed by cracking.
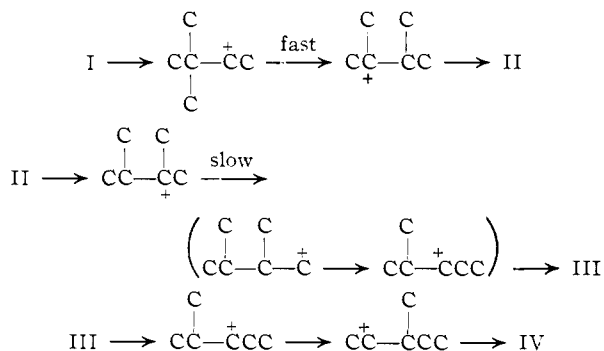
(17) L. G. Cannell and R. W. Taft, Jr., THIS JOURNAL, 78, 5812 (1956).

(18) F. C. Whitmore and P. L. Meunier, ibid., 63, 2197 (1941).

(19) F. C. Whitmore, W. S. Ropp and N. C. Cook, ibid., 72, 1507 (1950).

(20) L. Schmerling and V. N. Ipatieff in "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 21.

In agreement with a carbonium ion mechanism is also the fact that $k_1/k_2 = 10$. The reaction I → II involves the rearrangement of a secondary neopentyl type carbonium ion to a more stable tertiary carbonium ion and should proceed relatively fast, whereas the isomerization of II→III is visualized to proceed formally through an unstable primary carbonium ion and can be expected to be much slower.[3]

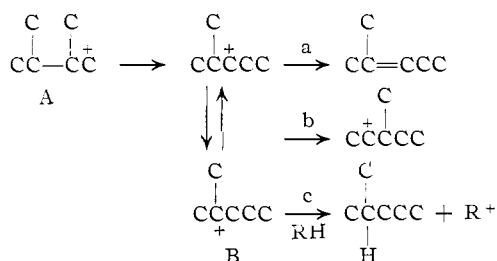$$I \longrightarrow C\overset{C}{C}-\overset{+}{C}C \xrightarrow{\text{fast}} C\overset{C}{\underset{C}{C}}-\overset{C}{\underset{+}{C}}C \longrightarrow II$$

$$II \longrightarrow C\overset{C}{C}-\overset{C}{\underset{+}{C}}C \xrightarrow{\text{slow}}$$

$$\left(C\overset{C}{C}-\overset{C}{C}-\overset{+}{C} \longrightarrow C\overset{C}{C}-\overset{+}{C}CC \right) \longrightarrow III$$

$$III \longrightarrow C\overset{C}{C}-\overset{+}{C}CC \longrightarrow C\overset{C}{\underset{+}{C}}-CCC \longrightarrow IV$$

Indeed, with certain acidic catalysts the reaction II → III is so slow relative to I → II, that II is the only product. For example, 3,3-dimethyl-1-butene (I) was converted to 2,3-dimethylbutene (II) exclusively over certain commercial alumina catalysts containing alkali,[3] over phosphorus pentoxide on silica gel,[21] and over aluminum sulfate.[4]

It is realized, however, that the relative ease of skeletal rearrangement of olefins depends not only on the rate of interconversion of isomeric carbonium ions, but also on the rate of formation of the carbonium ions and to some extent on the stability of the corresponding olefins. It is significant that the kinetic data indicate a series reaction: I → II → III → IV. This sequence is to be expected from a rearrangement of carbonium ions by 1,2- shifts of methyl groups. A direct formation of, say, 2-methylpentene from 3,3-dimethyl-1-butene (I) would require a 1,3 - shift which apparently does not take place.

The mechanism advanced for the isomerization of 3,3-dimethyl-1-butene is in essential agreement with that proposed for the isomerization of the corresponding saturated hydrocarbon by aluminum chloride–hydrogen chloride[22] and by hydrogen fluoride promoted by boron fluoride[23] which also proceed via carbonium ions. It is in sharp contrast, however, to the mechanism proposed for hexane isomerization over reforming catalysts[24] in which carbonium ion rearrangements by 1,3-shifts are invoked to account for a supposedly direct interconversion of 2,3-dimethylbutane and 3-methylpentane.

The consecutive rather than parallel nature of the isomerization reaction over alumina requires that regeneration of an olefin from a carbonium

ion by loss of a proton is faster than methyl migration. For example, after carbonium ion B is produced from A by methyl migration, it is released from the surface as the olefin (step a) at a rate faster than that of the competing methyl migration (step b).

$$C\overset{C}{\underset{}{C}}-\overset{C}{\underset{+}{C}}C \longrightarrow CCC\overset{+}{C}C \xrightarrow{a} C\overset{C}{C}=CCC$$

$$A \qquad \updownarrow \qquad \xrightarrow{b} C\overset{+}{\underset{}{C}}C\overset{C}{C}C$$

$$C\overset{C}{\underset{+}{C}}CCC \xrightarrow[RH]{c} C\overset{C}{\underset{H}{C}}CCC + R^+$$
$$B \qquad\qquad\qquad H$$

As a result, at a high flow rate (expt. 1) 2-methylpentene is formed without simultaneous formation of detectable amounts of 3-methylpentene. Even at a total conversion of 97.3% (expt. 2), the 2- and 3-methylpentenes were not equilibrated (Table III). This result can be contrasted with the isomerization of 2,2-dimethylbutane catalyzed by aluminum chloride–hydrogen chloride[22] which is believed to proceed by a carbonium ion chain mechanism. In this reaction, an equilibrium mixture of 2- and 3-methylpentane was obtained after only 4% of the starting material had reacted. Here the reaction competing with methyl migration (step b) is an intermolecular chain transfer (step c) which apparently proceeds more slowly than the methyl migration (b). A related observation has been made in the hydro-isomerization of ethylcyclohexane over a nickel–silica alumina catalyst.[25] The results of C^{14} tracer experiments indicated that many skeletal rearrangements of an adsorbed carbonium ion take place during a single residence period on the catalyst leading to thermodynamic and isotopic equilibration.

Isomerization of Butene.—Butene was isomerized by passing over 10 ml. of alumina catalyst at 230° at various flow rates. The effluent gases were analyzed directly by gas chromatography. Besides the n-butenes, the only other detectable compound was isobutylene in trace amounts. The results of the isomerization of 1-butene (A) over pelleted alumina are shown in Fig. 4. Similar experiments were performed with cis- (C) and with trans-2-butene (T) which are summarized in Fig. 5. Starting from each of the three isomers, the same equilibrium mixture is approached at longer contact times indicating that the reaction is reversible. From the tangents to the curves (Fig. 5) at low conversions[26] the initial product ratios were obtained (Table IV, col. 1).

It becomes apparent that starting with 1-butene (A) the thermodynamically less stable cis-2-butene (C) is produced at a faster rate than the trans isomer (T).

When the catalyst was used in the form of a powder rather than in pellets, the initial cis/trans ratio increased to 4.4 (Fig. 6) while the ratio of trans/1- stayed the same (Table IV, col. 2).

(21) K. C. Laughlin, C. W. Nash and F. C. Whitmore, THIS JOURNAL, **56**, 1395 (1934).

(22) B. L. Evering and R. C. Waugh, Ind. Eng. Chem., **43**, 1820 (1951).

(23) D. A. McCaulay, THIS JOURNAL, **81**, 6437 (1959).

(24) W. C. Starnes and R. C. Zabor, Paper presented before the Division of Petroleum Chemistry, American Chemical Society Meeting, April 5 10, 1959, Boston, Mass., abstracts p. A-23.

(25) H. Pines and A. W. Shaw, THIS JOURNAL, **79**, 1474 (1957).
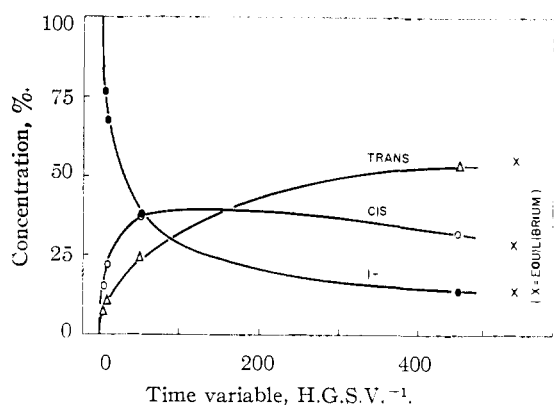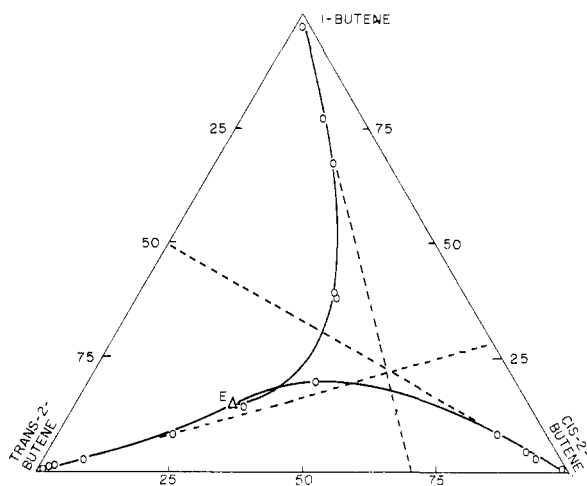
(26) It can be shown that the three tangents should intersect in one point which provides a test on the accuracy of the data.

Fig. 4.—Isomerization of 1-butene over alumina, $T = 230°$.

Fig. 5.—Isomerization of butenes over alumina at 230°;
E = equilibrium.

The ratio of the products at very low conversion is proportional to the ratio of the rate constants. Starting with each of the three n-butenes, the other two components are formed in parallel rather than consecutive reactions as indicated by the finite initial slopes in the concentration–time curves (e.g., Fig. 4).[27] This strongly suggests a three-

TABLE IV
EXPERIMENTAL INITIAL PRODUCT RATIOS AND EQUILIBRIUM
RATIOS

| | Catalyst | | |
	Pelleted	Powdered	Equil.[15]
cis/trans	2.4	4.4	0.53
cis/1-	2.5	4.4[a]	2.0
trans/1-	1.0	1.0	3.8

[a] Calculated from equation 4.

component kinetic system with competitive reversible reactions, as shown in Fig. 7. In this system, the rate ratios (and therefore, initial product ratios) are correlated by the equation

$$k_1 k_3 k_4 / k_3 k_2 k_6 = 1 \qquad (4)$$

The data in Table IV (col. 1) give a value of 1.04 which is within experimental error of the expected value of 1.00.

(27) It was suggested by Lucchesi, et al.,[7a] without sufficient experimental evidence and contrary to the present observation that the isomerization of 1-butene is irreversible and that trans-butene is formed solely from the cis isomer.
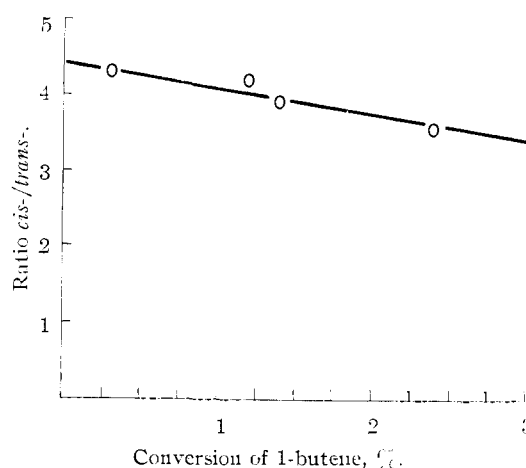
Fig. 6.—Isomerization of 1-butene over powdered alumina
at 230°.
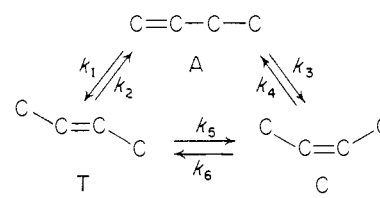
	k_1	k_2	k_3	k_4	k_5	k_6
Pellets	3.8	1.0	9.1	4.6	2.4	4.6
Powder	3.8	1.0	16.7	8.5	4.4	8.5

Fig. 7.—Apparent relative rate constants.

It was shown recently[7b] that the six relative rate constants (Fig. 7) can be obtained from the initial product ratios and the equilibrium values, if the reaction is kinetically simple. Application of this principle to the present data gives the apparent relative rate constants shown in Fig. 7.

The dependence of the apparent relative rates on the particle size of the catalyst might result from the fact that molecules formed in a pore of a large particle are more subject to secondary equilibration reactions before they appear in the gas phase as products than those in a small particle. Therefore, the values obtained with the powdered catalyst are considered to be more significant.

The operation of kinetic rather than thermodynamic product control in the alumina-catalyzed isomerization is unexpected. The observed rate ratio k_3/k_1 (4.4) is 8.3 times larger than the value of 0.53 which had been used previously on the assumption of thermodynamically controlled rates.[11] Similarly, C and T isomerize to A at quite different rates (8.5/1) contrary to beliefs expressed earlier.[12]

The observed stereoselectivity does not appear to be limited to alumina-catalyzed reactions. Preliminary experiments showed that over a silica–alumina catalyst 1-butene forms cis- and trans-2-butene in an initial ratio of at least 1.7 at 125°. That the presence of a solid surface is not a necessary condition is indicated by the data in Table V which show the results of the isomerization of 1-butene by liquid phosphoric acid. Again, the less stable cis-2-butene is formed faster than the trans isomer. Stereoselective olefin isomerization

TABLE V

ISOMERIZATION OF 1-BUTENE BY PHOSPHORIC ACID

Expt.	Temp., °C.	Reaction time, sec.	1-	Butene, % trans-2-	cis-2-	Ratio cis/trans
1	52	3	99.0	0.4	0.6	1.5
2	61	7	87.7	5.4	6.9	1.3
3	100	3	95.1	1.8	3.1	1.7
4	100	2	97.5	0.7	1.8	2.6
5[a]	35	7	89.0	5.2	5.8	1.1

[a] 4% silver oxide was added to the phosphoric acid.

thus is observed with liquid as well as with solid acid catalysts.

The significance of the rate data lies in the fact that they provide a criterion for establishing a mechanistic picture of the reaction. Several mechanisms have been advanced for the acid-catalyzed double bond isomerization. Ipatieff and Corson[28] proposed an addition–elimination mechanism in which the catalyst (H–X) adds to the double bond to form an ester intermediate which eliminates H–X again in a different direction. That this ester decomposition does not take place by a *concerted* mechanism appears from a consideration of two factors. First, esters, once formed, eliminate olefins thermally only at temperatures higher than those at which isomerization takes place. Secondly, from the cyclic transition state postulated for ester pyrolysis (Fig. 8) one predicts a faster rate for the formation of *trans*-2-
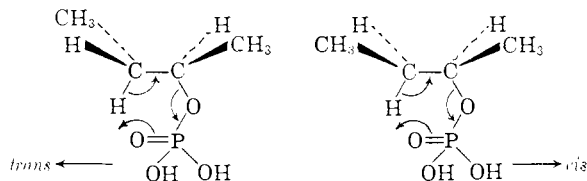

Fig. 8.—Transition state in ester decomposition.

butene relative to that of the *cis* compound since the *cis* transition state is of higher energy as a result of the non-bonded interaction of the two opposed methyl groups. This expectation was indeed verified by the pyrolysis of 2-butyl acetate,[29] but is not satisfied by the present data. Breakdown of the proposed ester intermediate by an ionic mechanism leads to a carbonium ion intermediate and will be discussed below.

Turkevich and Smith[11] have presented a different picture for the transition state. An activated complex between olefin and acid is formed in which the acid acts as both a donor and an acceptor of hydrogen atoms. The process of hydrogen transfer from one part of the molecule to another is visualized as taking place in "one elementary act," that is, in a concerted mechanism. This "hydrogen switch" mechanism, illustrated with phosphoric acid as a catalyst in Fig. 9, is said to be operative with catalysts such as alumina or phosphoric, sulfuric and perchloric acid. Attractive as it appears, it does not explain skeletal rearrangements which do occur with the same catalysts. Furthermore, it does not allow for a direct *cis–trans* interconversion which was now found to
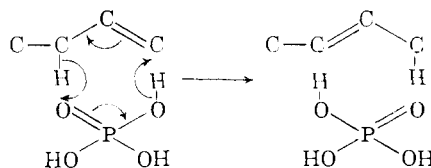

Fig. 9.—"Hydrogen switch" mechanism.

take place at an equal (for C) or even faster rate (for T) than double bond shift.

The similarity of rates for the two types of isomerization is indeed surprising. Migration of the double bond involves breaking of a carbon–hydrogen bond and formation of a new one, whereas *cis–trans* interconversion requires untying of a π-bond, that is, of a bond of quite different strength. It is therefore concluded that bond breaking is not occurring in the rate-determining step. The similarity of rates for positional and geometric isomerization suggests further that both reactions proceed by the same mechanism. A satisfactory one appears to be a conventional carbonium ion mechanism[30] with a common intermediate, the secondary butyl carbonium ion, for *cis–trans* as well as for 1,2-isomerization (Fig. 10). According
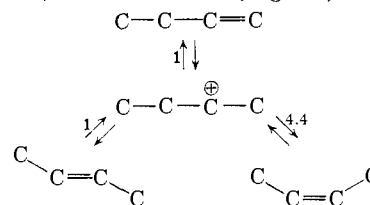

Fig. 10.—Carbonium ion mechanism; numbers indicate relative rates.

to this picture, the observed rate ratios (Table IV) reflect different rates of generating the various olefins from the carbonium ion which are designated by the numbers in Fig. 10. However, the mechanism, as it stands, is incomplete. An equal or faster rate for *trans*- as compared to *cis*-2-butene would be expected on the basis of statistical and steric or energetic considerations[31,32] whereas the opposite is found to be the case. This indicates that the transition state separating carbonium ion and olefin does not resemble the olefin.[33] To account for the observed rate data it is suggested that the elimination of a proton from the carbonium ion proceeds through the rearrangement to a π-complex[34–36] in a slow step with subsequent rapid loss of the proton (Fig. 11).[37] It is, of course,

(28) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **27**, 1069 (1935).

(29) H. Pines and W. O. Haag, *J. Org. Chem.*, **24**, 877 (1959).

(30) F. C. Whitmore, THIS JOURNAL, **54**, 3264 (1932).

(31) D. Y. Curtin, *Record. Chem. Prog.*, **15**, 111 (1954).

(32) D. J. Cram, C. D. Green and C. H. DePuy, THIS JOURNAL, **78**, 790 (1956).

(33) Application of Hammond's postulate (G. S. Hammond, *ibid.*, **77**, 334 (1955)) is in agreement with this conclusion since the reaction carbonium ion → olefin should be exothermic.

(34) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); *Bull. soc. chim. France*, **C75**, C86 (1951).

(35) C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 40.

(36) No distinction will be made in the present discussion between a proton π-complex and a bridged protonium ion; see S. Winstein and N. J. Holmes, THIS JOURNAL, **77**, 5572 (1955); L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956).

(37) R. W. Taft, Jr., and co-workers (*ibid.*, **77**, 1584 (1955); **78**, 5807 (1956); **79**, 3724 (1957)) have presented evidence that the reverse reaction—addition of a proton to an olefin to give a carbonium ion—similarly proceeds *via* a π-complex.
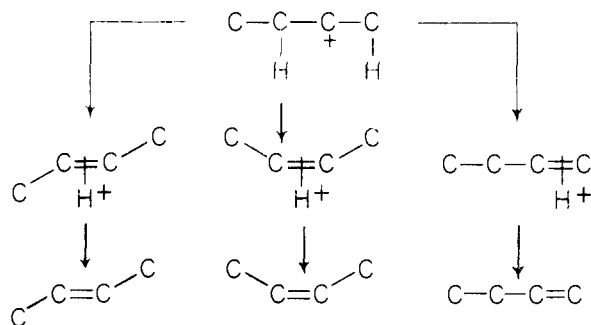
Fig. 11.—Loss of proton from carbonium ion via π-complex.

possible that the formation of the π-complex occurs *during* the formation of the carbonium ion.[38] To the extent that the transition states are ap-

proximated by the π-complexes (Fig. 11) it appears that the energies of the π-complexes are *cis* < *trans* = 1-butene. It is interesting to note that *cis*-olefins form more stable π-complexes with silver ions[39,40] than the corresponding *trans*-olefins. Recent studies on hydrogen bonding to olefins[41-43] have shown that 2-olefins (apparently mixture of *cis*- and *trans*-) are stronger bases than 1-olefins and form stronger hydrogen bonds. Thus, the relative stabilities of the π-complexes, and therefore the relative rates of formation of the olefins, seem to be governed by the basicities of the corresponding olefins.

(38) Neighboring hydrogen participation in the formation of carbonium ions by ionization has been demonstrated recently: W. B. Smith, R. E. Bowman and Th. J. Kmet, This Journal, **81**, 997 (1959); D. J. Cram and J. Tadanier, *ibid.*, **81**, 2737 (1959); S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

(39) F. R. Hepner, K. N. Trueblood and H. J. Lucas, This Journal, **74**, 1333 (1952).

(40) P. D. Gardner, R. L. Brandon and N. J. Nix, *Chemistry & Industry*, 1363 (1958).

(41) A. W. Baker and A. T. Shulgin, This Journal, **80**, 5358 (1958).

(42) P. V. R. Schleyer, D. S. Trifan and R. Bacskai, *ibid.*, **80**, 6691 (1958).
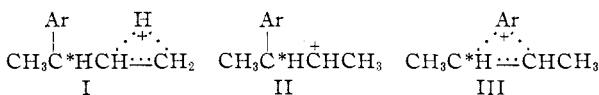
(43) R. West, *ibid.*, **81**, 1614 (1959).

The Reactions of 3-Phenyl-1-butylamine-3-14C and 3-p-Anisyl-1-butylamine-3-14C with Nitrous Acid[1,2]

By Arthur W. Fort and Robert E. Leary

The diazotization of 3-phenyl-1-butylamine-3-14C in acetic acid gives 3-phenyl-1-butene, 3-phenyl-1-butyl acetate and diastereoisomeric 3-phenyl-2-butyl acetates. 3-p-Anisyl-1-butylamine-3-14C gives a similar product mixture. The secondary ester products of these reactions show extensive isotope-position rearrangement. The significance of these results is discussed.

The reactions of 3-phenyl-1-butylamine-3-14C and 3-p-anisyl-1-butylamine-3-14C with nitrous acid have been investigated with the objective of identifying the intermediates leading to secondary products in these and similar reactions. In the present work information was sought concerning the relative importance of the possible intermediates I, II and III.

$$\underset{I}{\underset{CH_3C^*HCH=CH_2}{\overset{Ar\qquad H}{\big|\quad\cdot\overset{+}{\cdot}\cdot}}} \qquad \underset{II}{\underset{CH_3C^*HCHCH_3}{\overset{Ar}{\big|\quad\overset{+}{}}}} \qquad \underset{III}{\underset{CH_3C^*H=CHCH_3}{\overset{Ar}{\cdot\overset{+}{\cdot}\cdot}}}$$

Ar = C₆H₅– or p-CH₃OC₆H₄–

The symmetrical aryl-bridged ions III, if formed, will lead to secondary products showing isotope-position rearrangement. Secondary products formed by solvent attack on intermediates I and/or II will not show isotope-position rearrangement.

The reaction of 3-phenyl-1-butylamine-3-14C with sodium nitrite in glacial acetic acid gave 3-phenyl-1-butene-X-14C (IV), 10%, and a mixture of phenylbutyl-X-14C acetates, which, after treatment with lithium aluminum hydride and distillation at reduced pressure, gave a 63% yield (based on unrecovered amine) of phenylbutanols. The ratio of alcohol products, estimated by gas chroma-

tography, was 62 ± 2% 3-phenyl-1-butanol-X-14C (V), 28 ± 2% erythro-3-phenyl-2-butanol-X-14C (VI) and 10 ± 2% threo-3-phenyl-2-butanol-X-14C (VII). Other isomeric phenylbutanols were not detected. The alcohol mixture was separated by fractional distillation into V and a mixture of the diastereoisomers VI and VII, from which pure erythro-3-phenyl-2-butanol was obtained by the procedure of Cram.[3] The absence of the conjugated olefins, cis-2-phenyl-2-butene and trans-2-phenyl-2-butene, from the crude olefin product was established by gas chromatography and by the similarity of its infrared spectrum with that of authentic 3-phenyl-1-butene. A control experiment showed that the conjugated olefins would have survived the reaction conditions, in large part, if they had been formed.

Isotope-position rearrangement attending the formation of products in the deamination reaction of 3-phenyl-1-butylamine-3-14C was determined by oxidizing each product to benzoic acid and comparing the 14C-activity of the benzoic acid fragment with that of its parent compound. The measured 14C-activities and percentage rearrangements are given in Table I.

The reaction of 3-p-anisyl-1-butylamine-3-14C with sodium nitrite in acetic acid gave a product mixture that was similar to the one obtained from

(3) D. J. Cram, This Journal, **71**, 3863 (1949).