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Stereoselective Catalytic Isomerization of *n*-Butenes

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Following the recent observations of stereoselectivity in the catalytic isomerization of butene-1, the isomerization of *n*-butenes has been studied on a wide variety of catalysts. The stereoselective isomerization of butene-1 has been found to occur to a smaller or greater extent on all the catalysts studied. The highest selectivities were found on the basic catalysts and the smallest on some metals. The butene-2 isomerization has been observed to proceed by exclusive double bond shift (on some basic catalysts, *e.g.*, KOH) or exclusive *cis/trans* conversion (on some acidic catalysts, *e.g.*, H_2SO_4) or by combination of the two processes.

Introduction

The isomerization reactions of the *n*-butenes have been the subject of study for many years,[2] and both the thermal[3–5] and catalytic[6–10] processes have been investigated. In the previous literature there have been some indications of a stereoselectivity in the catalytic reaction of butene-1,[11,12] but only very recently has this aspect been studied. Three pieces of independent work on this subject have been reported in the last two years: (1) Lucchesi, *et al.*,[13] using butene-1 on a silica–alumina catalyst; (2) Haag and Pines[14] using butene-1, with some work with butene-2 isomers, on alkali metal and acidic catalysts; and (3) Cvetanović and Foster[15] using the three *n*-butene isomers on a series of NiO/Cr_2O_3 catalysts. Lucchesi, *et al.*, found a very marked stereoselectivity favoring the formation of *cis*-butene-2 by a ratio of 4 to 1 at 20% reaction, this ratio increasing rapidly at lower conversions. This it was felt was not consistent with the usually accepted carbonium ion mechanism and the formation of a π-complex between the double bond and the surface proton was suggested. The results of Haag and Pines show a similar marked selectivity on supported alkali metal catalysts and a less marked selectivity on the acid catalysts. *cis*- and *trans*-butene-2 were also used as initial reactant in some cases and from the data obtained the relative rates of the six isomerization reactions were calculated. The selectivity of the base-catalyzed anionic reaction was attributed to a preferential attack on the *cis* form of the allylic anion, but its occurrence in the acid-catalyzed cationic reaction was found difficult to rationalize. The previous work in these laboratories using a series of catalysts varying in composition from 0 to 100% NiO in Cr_2O_3 showed that the stereoselectivity was greatest on the catalysts containing approximately equimolar quantities of the two oxides and consisting mainly of $NiCr_2O_4$, decreasing when a large excess of either oxide was present. The impregnation of any of these catalysts with KOH solution produced a highly selective catalyst.

The present work was undertaken with the object of establishing how general the selectivity in the catalytic butene isomerization is and whether a broad generalization can be drawn relating the catalyst type and the extent of the selectivity. For this purpose interconversions of the three *n*-butenes have been studied on a wide variety of catalysts. The work has been mainly limited to small conversions in order that the initial ratios of the isomers formed can be obtained by extrapolation.

Experimental

The apparatus used was a circulatory flow system with a total volume of approximately 1.5 l. and a catalyst cell volume of 20 cc. The flow rate throughout was 1.8 l./hr at N.T.P. and the initial butene pressure 10 cm. Most of the catalyst materials were formed into 0.25″ cylindrical pellets and a charge of approximately 15 g. taken in each case.[16] Each catalyst was used at the lowest possible temperature to obtain results at low % conversions. Samples of the gas exiting from the reactor were withdrawn at intervals and analyzed by gas chromatography, using a 50-ft. column of dimethylsulfolane on firebrick at room temperature. This gave a complete separation of the

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(1) National Research Council Postdoctorate Fellow, 1957–1959. Issued as N.R.C. Publication No. 5722.

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

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(4) G. B. Kistiakowsky and W. R. Smith, *ibid.*, **58**, 766 (1936).

(5) W. F. Anderson, *et al.*, *ibid.*, **80**, 2384 (1958).

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

(7) G. H. Twigg, *Proc. Roy. Soc. (London)*, **A178**, 106 (1941).

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

(9) J. Turkevich and R. K. Smith, *ibid.*, **16**, 466 (1948).

(10) T. I. Taylor and V. H. Dibeler, *J. Phys. Colloid Chem.*, **55**, 1036 (1951).

(11) H. H. Voge, G. M. Good and B. S. Greensfelder, *Ind. Eng. Chem.*, **38**, 1033 (1946).

(12) M. H. Polley, W. D. Schaeffer and W. R. Smith, *Can. J. Chem.*, **33**, 314 (1955).

(13) P. J. Lucchesi, D. L. Baeder and J. P. Longwell, THIS JOURNAL, **81**, 3235 (1959).

(14) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958); W. O. Haag and H. Pines, Symposium on Isomerization and Related Processes, Am. Chem. Soc. Meeting, Boston, April 5-10, 1959.

(15) R. J. Cvetanović and N. F. Foster, *Discussions Faraday Soc.*, **28**, 201 (1959).

(16) Some details of catalyst preparation are: KOH (AR grade) was heated above its melting point to remove the water; it was then allowed to solidify and was broken into fragments (approximately 0.25″ diameter) which were placed in the reactor at 320° and pumped immediately to minimize water uptake. An almost saturated solution of AR grade NaOH in distilled water was poured into a reaction cell packed with glass beads and then allowed to drain off until no more liquid dripped out; the cell was then attached to the apparatus, heated and pumped to remove excess water. LiOH and CaO powders (AR grade) were compressed into 0.25″ cylindrical pellets. K_2CrO_4 was pelleted similarly but with the addition of a few per cent. graphite as binding agent which was subsequently burned off by heating in a muffle furnace to just below the melting point of K_2CrO_4. The carbon used was "Carbon Decolorizing" from Fisher Scientific Co. which was compressed into 0.25″ pellets. Concentrated phosphoric and sulfuric acids were poured over glass beads packed in the reactor and time allowed for drainage as in the case of NaOH, with subsequent heating and pumping. Nickel (powder) and silver (shot) were compressed into 0.25″ pellets. Cr_2O_3 (AR grade), ZnO (AR grade) and Firebrick powder were each mixed with a few per cent. graphite and compressed into 0.25″ pellets which were then fired at 900° for 3–4 hours to burn off the carbon. The remaining catalysts (Clay, Esso, Davison and Alcoa) were obtained already activated and were formed into 0.25″ pellets without the addition of graphite and used without any pretreatment other than the usual pumping overnight (the standard procedure with all catalysts) prior to doing a run.

n-butene isomers. The butene isomers used were Phillips research grade.

Results

The data given in the accompanying tables were obtained from analyses of samples containing only the *n*-butenes, *i.e.*, from runs in which isomerization was the only reaction. The ratio between the two isomers produced by the reaction was calculated for each sample and plotted against the corresponding % conversion of the react antisomer. The ratio at zero conversion was obtained by extrapolation, giving the relative reaction rates for the formation of the two isomers.[17] In Table I the observed ratios and % conversions are given for some of the more interesting catalysts.

TABLE I

RATIOS OF THE ISOMERS FORMED AT DIFFERENT CONVERSIONS

	Reactant					
	Butene-1		*cis*-Butene-2		*trans*-Butene-2	
Catalyst	%^{a}	Ratio^b	%^{a}	Ratio^c	%^{a}	Ratio^d
KOH (320°)	1.5	0.11	1.3	0	0.68	0
	1.77	.086	1.7	0	1.25	0
	2.2	.235	2.2	0	2.75	0
	5.0	.37	5.6	0.037	5.63	0.23
	5.35	.35	15.7	.19	11.3	.49
	12.7	.33	22.3	.21	25.8	.8
	13.7	.33	40.5	.44	39.8	1.1
	26.1	.51	56.5	1.06		
	41.3	.50				
	64.9	.66				
	72.2	1.04				
H_3PO_4 (150°)	2.16	0.98	2.6	4.53	2.0	7.2
	7.3	1.06	5.11	4.5	7.3	4.15
	18.1	1.07	14.2	4.38	13.8	3.95
			19.2	4.5		
LiOH (440°)	3.12	0.6	4.2	0.075	2.14	0.09
	4.02	.51	12.9	.11	9.1	.17
	17.95	.59	23.0	.18	12.7	.21
	34.8	.64				
Alcoa (300°)	2.73	.86	13.4	112	9.25	150
	5.15	.96	22.4	50	15.25	169
	10.0	1.23	43.4	26	35.5	30
			52.5	19	39.3	20
Activated clay (40°)	4.51	0.86	6.91	1.37	7.35	2.15
	6.73	.98	9.47	1.65	16.02	3.37
	22.0	.95			20.4	4.1
	45.5	.92				
	50	.98				
	78.3	1.2				
Activated clay (200°)	11.8	1.25	9.66	2.68	7.37	2.03
	32.7	1.41	21.5	2.61	15.47	1.74
	63.8	1.43	41.6	2.9	26.7	2.7
	78	1.57	61.7	3.4	48.1	2.4
Nickel (300°)	9.8	1.49	3.1	1.82	2.0	<0.1
	17	1.49	4.13	1.3	2.76	.154
	30	1.51	9.25	0.88	5.62	.456
					10.74	.585

^{a} Percentage conversion. ^{b} *trans*/*cis*. ^{c} *trans*/butene-1 ^{d} *cis*/butene-1.

The extrapolated zero conversion ratios for all of the catalysts used are given in Table II, together with the selectivity factors obtained by taking into account the literature values[18] of the corresponding equilibrium ratios. The selectivity factor with respect to one of the two isomers (a, b) produced is defined as

$$S_a = \left(\frac{a}{b} \times \frac{b_e}{a_e} - 1\right) \Big/ \left(\frac{a}{b} \times \frac{b_e}{a_e} + 1\right) = -S_b$$

where a/b is the zero conversion ratio and a_e/b_e the corresponding equilibrium ratio. A selectivity factor $S_a = 1$ means exclusive formation of a, $S_a = 1$ exclusive formation of b, and $S_a = 0$ formation of the two isomers in their equilibrium ratio at the particular temperature. In Table II, for butene-1, a represents the *cis* isomer, and for both 2-butenes a represents butene-1.

Discussion

Examination of the selectivity factors in Table II for those catalysts used at more than one temperature, *e.g.*, activated clay, shows that the factors are temperature dependent, approaching zero as the temperature increases. A similar trend is observed in the results of Haag and Pines. This temperature dependence prevents strict comparison between selectivity factors for catalysts used at widely different temperatures. As can be seen from the table, the selectivity varies widely for each reactant isomer. In the butene-1 column values range from nearly unity for KOH to approaching zero for the metals Ni and Ag. No negative or zero values were found, showing that all the catalysts employed give rise to a more or less selective isomerization of butene-1, initially favoring the formation of *cis*-butene-2. In the *cis*-butene-2 column, the factors range from unity for KOH to −1 for H_2SO_4, showing a complete range of reaction courses from exclusive double bond shift to exclusive *cis–trans* isomerization. Similar variations from +1 to −1 are observed with *trans*-butene-2 as the reactant, and here again KOH has a selectivity factor of +1 and H_2SO_4 of −1.

The results in Table II show that catalytic isomerization of *n*-butenes occurs in general in a selective manner. Although there is essentially a complete range between the extreme cases, it appears possible to separate broadly the basic and acidic catalysts into two distinct groups, the extreme representatives of which are KOH and H_2SO_4. The former induces initially exclusive formation of *cis*-butene-2 from butene-1 and of butene-1 from either *cis*- or *trans*-butene-2. Sulfuric acid, on the other hand, shows a less pronounced selective formation of *cis*-butene-2 from butene-1 and initially exclusive *cis–trans* isomerization rather than a double bond shift. In Table III the fractions (f) of the isomers formed, with due allowance for the corresponding equilibrium ratios (taking $f_a = 1/(1 + ab_e/ba_e)$), are shown for some typical basic and acidic catalysts and there appears to be a significant distinction between the two groups. The factors calculated from the results of Haag and Pines are included for comparison. The change in behavior of firebrick after acid pretreatment, as shown in Table II, is largely in agreement with the general trends on basic and acidic catalysts.

The two metals studied, Ni and Ag, appear to form a distinct group. They give almost nonselective isomerization of butene-1 but essentially complete double bond shift in the case of *trans*-butene-2. *cis*-Butene-2 behaves similarly on silver, but this is less pronounced on nickel. Previous preliminary work in these laboratories suggests

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[17] Extrapolations in some cases were rather uncertain, but the data are, in general, adequate for the comparative discussion in the present paper.

[18] J. E. Kilpatrick, *et al.*, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

TABLE II

INITIAL ISOMER RATIOS AND SELECTIVITY FACTORS

Catalyst	Temp., °C.	Extrapolated zero conversion ratios[i] Butene-1	*cis*-Butene	*trans*-Butene	Selectivity factors Butene-1	*cis*-Butene	*trans*-Butene
KOH	320	<0.1	0	0	0.89 to 1.00	1.00	1.00
NaOH	400	0.47	<0.05	0.45	0.55	0.994 to 1.00	0.42
LiOH	440	0.6	0.05	0.07	.45	0.94	0.87
CaO	200	.3	....	0	.74	..	1.00
K_2CrO_4[a]	350	.28	0	..	.71	1.00	..
	400	.4	0.47	..	.60	0.59	..
Firebrick[b]	300	.4	..	..	.63	..	..
	350	..	0.23	..	..	0.80	..
	400	.84	.29	<0.1	.32	.73	0.83 to 1.00
Acid firebrick[c]	400	.6	.4	>2	.46	.64	−0.3 to −1.00
Vicor[d]	100	.76	.75	1.4	.53	.11	0.48
Cr_2O_3	250	.73	.7	0.9	.43	.67	.33
Carbon	250	.85	2.25	2.4	.37	.20	− .14
ZnO	550	.7	1.4	..	.37	− .18	..
Clay[e]	40	.93	0.8	1.2	.55	.92	.65
	200	1.23	2.5	4.8	.23	.28	.13
Esso[f]	50	0.72	..	..	.61	..	..
	75	.94	0.9	..	.49	.87	..
	100	..	..	2.5	..	..	.23
Davison[g]	35	.63	1.2	..	.68	.89	..
	100	..	..	3.8	..	..	.03
Alcoa[h]	300	.77	>200	>200	.39	−0.97 to −1.00	−0.99 to −1.00
H_3PO_4	150	.94	4.5	~10	.39	0.18	~− .5
H_2SO_4	30	1.1	∞	∞	.50	−1.00	−1.00
Nickel + H_2	300	1.5	2.0	<0.1	.07	0.14	.87 to 1.00
Silver	375	1.27	0.2	0	.13	0.82	1.00

[a] Decomposed to KOH and Cr_2O_3. [b] Fisher column pack firebrick. [c] Firebrick pretreated with HCl and washed. [d] Vicor porous glass, 96% silica. [e] P.M.C. activated clay. [f] Esso synthetic silica–alumina. [g] Davison silica–alumina (11% alumina). [h] Alcoa activated alumina. [i] Ratios as in Table I.

TABLE III

COMPARISON OF TYPICAL BASIC AND ACIDIC CATALYSTS AND OF METALS (Ni AND Ag)[b]

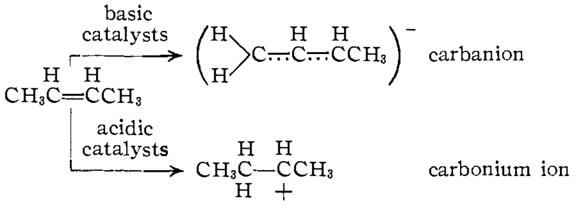
Catalyst	Temp., °C.	Butene-1 ↙ *trans*	Butene-1 ↘ *cis*	*cis*-Butene-2 ↙ *trans*	*cis*-Butene-2 ↘ butene-1	*trans*-Butene-2 ↙ *cis*	*trans*-Butene-2 ↘ butene-1
		A. Basic catalysts					
KOH	320	<0.06	>0.94	0	1.00	0	1.00
NaOH	400	.22	.78	0	1.00	0.29	0.71
LiOH	440	.27	.73	0.03	0.97	0.07	0.93
CaO	200	.13	.87	..	..	0	1.00
Na/Al_2O_3[a]	37	.08	.92	0.03	0.97	0.33	0.67
		B. Acidic catalysts					
H_2SO_4	30	0.25	0.75	1.00	0	1.00	0
H_3PO_4	150	.31	.69	0.41	0.59	0.77	0.23
Alcoa	300	.25	.75	1.00	0	1.00	0
Act. clay	200	.39	.61	0.36	0.64	0.44	0.56
H_3PO_4[a]	50	~ .18	~ .82	..	..	..	..
Al_2O_3[a]	230	.18	.82	0.21	0.79	0.56	0.44
		C. Metals					
Ni + H_2	300	0.46	0.54	0.43	0.57	<0.07	>0.93
Ag	375	0.44	0.56	0.09	0.91	0	1.00

[a] Haag and Pines, ref. 14. [b] The fractions of isomers formed have been corrected by allowing for the equilibrium ratios at the particular temperature.

that Fe, Co, Mn and Cr behave in a somewhat similar manner. In accordance with previous findings, the presence of hydrogen was found to be necessary to promote isomerization on nickel. With silver this appeared not to be the case.

The high selectivity of the base-catalyzed reaction has an interesting parallel in the polymerization of styrene by Ziegler type catalysts.[19] These catalysts may be formed with either basic or acidic properties according to the conditions used. The acidic catalysts produce an atactic (randomly oriented) polymer by a cationic mechanism while the basic catalysts yield an isotactic (highly oriented) polymer by an anionic mechanism, *i.e.*, the basic catalyst gives a highly stereoselective reaction.

Attempts have been made to interpret the selectivity of the butene-1 isomerization in terms of both the carbonium ion mechanism usually postulated for acid-catalyzed reactions[13,14] and the carbanion mechanism associated with base-catalyzed reactions.[14] Sufficient data are not yet available to allow any further expansion of the ideas already put forward, but as has been previously pointed out,[14] the base-catalyzed reaction proceeding *via* a highly unsaturated carbanion might be expected to exhibit a greater stereoselectivity, as is observed in the present work, due to the restriction on rotation which is not present in the almost fully saturated carbonium ion.



The very pronounced differences in reaction course observed in present work with *cis*- and

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(19) F. Dannusso, *et al. Chim. e Ind.*, **41**, 13 (1959).

trans-butene-2 on acidic and basic catalysts could also be attributed to the lack of free rotation in the carbanion.

The unsaturation of the carbanion 2–3 bond could hinder rotation so that return of a proton on either the 1- or 3-carbon atom would result in the formation of butene-1 or reformation of the original reactant butene-2 isomer. The allylic carbanion is likely to retain the steric configuration of the reactant butene-2 isomer and the formation of the other butene-2 isomer would require its rearrangement. The freedom of rotation about the corresponding bond in the carbonium ion would allow the formation of either of the butene-2 isomers thus permitting the energetically more favorable *cis–trans* isomerization to proceed. Butene-1 formation from the carbonium ion will also be possible and will become more important as the temperature increases.

In the discussed mechanisms the intermediate carbonium and carbanions are formally treated as entirely free. Under such conditions it could be expected that all acid catalysts should exhibit the same stereoselectivity at the same conversion and temperature and this should hold also for the basic catalysts.[20] Although it has not been possible in the present work to standardize the experimental conditions and it is therefore difficult to make with certainty comparisons of this kind, there appear to be appreciable individual differences between various catalysts at roughly comparable conditions. Some of these may perhaps be due to duality of character of the catalysts, either as an inherent property of the catalytic material or due to gross inhomogeneities. Also, the intermediate ionic species must be influenced to some extent by the proximity of or direct complexing with the catalyst and the degree of charge transfer is likely to differ in different catalysts. Finally, purely geometric factors[9,15] could come into play to some extent although they are, in general, not likely to play a decisive role in view of the broad distinctions observed in the present work which appear to be primarily associated with the acidity and basicity of the catalytic materials.

The behavior of the metals Ni and Ag cannot be discussed with any certainty. Either the dissociative mechanism or the hydrogen switch mechanism of Turkevitch and Smith[4] would predict lack of selectivity in the butene-1 isomerization and essentially exclusive double bond shift with the two butene-2 isomers, as is observed in the case of silver. The associative mechanism, on the other hand, might be expected to permit easy *cis–trans* isomerization.

[20] Pointed out by one of the referees of the present work.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., TEXAS CITY, TEX.]

The Reaction of Styryl Radicals with Organoaluminum Compounds

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The chain transfer constants of organoaluminum compounds with the styryl radical have been measured. These transfer constants were found to be unusually large The mechanism appears to be one of radical exchange between the whole group attached to the aluminum atom and the attacking styryl radical.

Introduction

A large number of compounds have been found to be active as transfer agents with free radicals.[1] All of these compounds have a common mode of reaction, the transfer of a single atom to the attacking radical with the generation of a new free radical[2]

$$R_1X + R\cdot_2 \longrightarrow R_2X + R\cdot_1$$

where $R\cdot_1$ and $R\cdot_2$ are free radicals derived from the respective molecules and X is an atom such as H or a halide. Transfer by disulfides may be an exception to this rule.[3] The purpose of this paper is to report a transfer reaction involving a whole group instead of a single atom. The process may be viewed as a radical exchange. The transfer agents are organoaluminum compounds whose reactions with free radicals have not been reported previously. Styrene was used as the monomer.

Results

Chain Transfer Constants.—Representative data are shown in Fig. 1 on a Mayo-type plot[4] for triisobutylaluminum. An example of the primary data from which Fig. 1 was derived is shown in Table I.

TABLE I

PRIMARY DATA AT 110°

Molar ratio of triisobutylaluminum to styrene (× 10⁴) 1.11		6.02		10.3	
Time,[a] hours	D.P.[b]	Time, hours	D.P.	Time, hours	D.P.
1.24	1010	0.65	89	0.92	57
2.10	1050	1.29	112	2.22	57
3.18	1035	1.91	152	2.50	76

[a] Time after immersing tube in constant temperature bath. [b] Degree of polymerization.

The chain transfer constant, as computed by least squares, is 28.5. This value remains unchanged over the temperature range of 85 to 110°, giving a value of 6–8 kcal. for the activation energy for the transfer reaction.[5] It is to be noted that the value of the degree of polymerization obtained with no transfer agent present, $(D.P.)_0$, has been ignored in these calculations. The justification for doing this is that the transfer agent is destroyed by reaction with impurities in the monomer when

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[1] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 148–161.

[2] Page 154 of ref. 1.

[3] A. V. Tobolsky and B. Baysal, THIS JOURNAL, **75**, 1757 (1953).

[4] F. R. Mayo, *ibid.*, 2324 (1943).

[5] R. H. Boundy and R. F. Boyer, "Styrene—Its Polymers, Copolymers and Derivatives," Reinhold Publ. Corp., New York, N. Y., 1952, p. 238.