

## Tracer Studies of Acid-Catalyzed Reactions

### IV. Rate Constants for *n*-Butene Interconversion Reactions over Alumina, Fluorided Alumina, and Silica-Alumina

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Received June 10, 1966; revised August 6, 1966

$C^{14}$  tracers were used to determine the relative rate constants for *n*-butene interconversion reactions over alumina, fluorided alumina, and silica-alumina in a micro-catalytic apparatus, and it was established that these reactions are all first order in the reactants. Over silica-alumina, 1-butene was isomerized about equally to *cis*- and *trans*-2-butene, while *cis*-2-butene was isomerized to the *trans* isomer only slightly faster than to 1-butene. The order of reactivity was 1-butene > *cis*- > *trans*-2-butene. Over alumina, 1-butene was isomerized to *cis* about twice as fast as to the more stable *trans* isomer, while *cis*-2-butene was converted to *trans* much faster than to 1-butene. The overall reactivities followed the order: 1-butene  $\approx$  *cis*- > *trans*-2-butene. Fluoriding alumina altered the selectivities markedly, the most noticeable effects being higher *cis/trans* and 1-butene/*trans* ratios.

The amount and lability of residues which were deposited on these catalysts were also investigated. "Tail gas" (steady state flow) experiments yielded information concerning poisoning and selectivity changes during 1-butene isomerization which resulted from fluoriding aluminas. A method for obtaining good yields of radioactive *cis*-2-butene from  $C^{14}$  1-butene is reported.

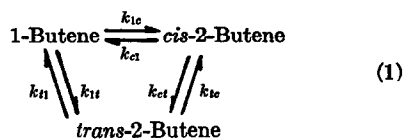
#### INTRODUCTION

The puzzling problem of the selectivity of oxide catalysts in the isomerization of 1-butene has been recognized for some years, although in the earliest work (1-4) it was supposed that the 2-butenes were formed in thermodynamic equilibrium. Pines and Haag (5) noted the stereoselectivity in the isomerization over sodium dispersed on alumina, and Lucchesi *et al.* (6) reported that the thermodynamically unfavored *cis*-2-butene was kinetically favored in 1-butene isomerization over silica-alumina. Since then, a number of investigators (7-16) have found such catalyst-dependent selectivity to be quite general over most oxides. The present situation has been recently reviewed by Gerberich and Hall (16).

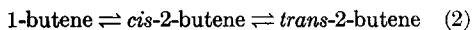
Although several mechanisms for the double-bond and *cis-trans* isomerizations

have been suggested in the literature, none seems to be completely consistent with all the data. It is entirely possible that no single mechanism can be applied generally to all oxide catalysts. The overall objective of this series of papers (16-19) was to provide additional information which may be helpful in elucidating the mechanisms which are involved, through the use of tracers.

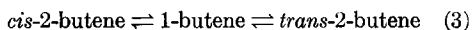
Some of the proposed mechanisms predict that one of the three possible reaction paths for interconversion among the three *n*-butenes does not exist, i.e., that a pair of rate constants in the scheme



is vanishingly small. For example, the mechanism of Lucchesi, Baeder and Longwell (6) necessarily implies that the direct conversion of 1-butene to *trans*-2-butene does not occur over silica-alumina, but that *trans*-2-butene is formed according to the scheme



On the other hand, Leftin and Hermans (15) concluded that over another silica-alumina catalyst *cis*-*trans* interconversion reactions did not take place and that the *trans*-2-butene must be formed from the *cis* isomer through the intermediate 1-butene, viz.,



These and similar schemes can be ruled out if it can be shown that all possible reaction paths are significant.

It must be recognized that the analysis used herein, based on Eq. (1), implicitly assumes that the surface reaction is rate-controlling. If desorption of products were slow compared with the surface reaction, the butenes could reach thermodynamic equilibrium on the surface and desorb accordingly. Whereas the equilibrium ratios on the surface need not be identical with those in the gas, it seems unlikely that they would be inverted, or that *cis*-2-butene would desorb selectively over *trans*-2-butene as required by the available data. Moreover, since the surface equilibrium condition would be somewhat different for every catalyst, generalities would not be expected among catalysts of a particular type, but which had been made in different ways or differed substantially in purity or in degree of poisoning. In the present work, C<sup>14</sup> tracers and a microcatalytic reactor were employed to determine quantitatively all the six relative rate constants for the *n*-butene interconversion reactions and to investigate the amount and lability of "residues" which are deposited on alumina, fluorided alumina, and silica-alumina catalysts. Some "tail gas" (steady state flow) experiments were also performed to obtain information about poisoning and selectivity

changes which occur during the isomerization of 1-butene over fluorided aluminas.

## EXPERIMENTAL

The experimental procedures can be divided into two main categories. The first involved three variations of the microcatalytic technique (17, 20), two including C<sup>14</sup> tracers, to determine quantitatively the relative rate constants for *n*-butene isomerization over several alumina, fluorided alumina, and silica-alumina catalysts. The second combined both microcatalytic and flow experiments to survey the catalytic behavior of fluorided aluminas for the isomerization of 1-butene.

**Microcatalytic procedures.** Catalyst samples (0.03–0.60 g) were sealed into Pyrex microreactors connected through glass joints to an apparatus described elsewhere (21). Helium carrier gas, purified by passage through a charcoal trap at –195°C, was flowed over the catalyst at 28 cc(NTP)/min and at about 2 atm pressure. Measured amounts (6–8 cc) of premixed reactants were introduced into the helium stream by manipulation of stopcocks connected to a gas-handling system. The products were first collected for 30 min in a –195°C trap before being flash-evaporated into the chromatographic column (30 ft of 2:1 dimethylsulfolane:hexamethylphosphoramide on firebrick) kept at 0°C; base-line resolution among the three *n*-butenes resulted. When C<sup>14</sup> tracers were used, the separated compounds were each collected in –195°C traps for radioactivity analysis.

The three microcatalytic procedures used were designated M-1, M-2, and M-3. M-1 consisted of passing slugs of either 1-butene with a trace of radioactive *cis*-2-butene-C<sup>14</sup>, or *cis*-2-butene with a trace of radioactive 1-butene-C<sup>14</sup>, over each of the catalysts under conditions where conversion was low (e.g., considerably less than 10%). Each of the three *n*-butenes was trapped and subjected to analysis for radioactivity; both specific and total activity in each product could be calculated from these measurements. An example of these data is given in Table 1.

In the M-2 experiments, slugs of 1:1

TABLE 1  
RESULTS FROM AN M-1 EXPERIMENT: THE ISOMERIZATION OF *cis*-2-BUTENE CONTAINING A TRACE OF 1-BUTENE, 1-C<sup>14</sup> OVER FLUORIDED ALUMINA, FA-1.2, AT 51°C<sup>a</sup>

Slug No.	Amt. butenes in products [cc(NTP)]			Specific activity of products (c min <sup>-1</sup> cc <sup>-1</sup> × 10 <sup>-4</sup> )			Total activity of products (c min <sup>-1</sup> × 10 <sup>-4</sup> )			Ratio sp. act. <i>trans</i> / <i>cis</i> /But-1	Ratio total act. <i>cis</i> / <i>trans</i>
	But-1	<i>trans</i>	<i>cis</i>	But-1	<i>trans</i>	<i>cis</i>	But-1	<i>trans</i>	<i>cis</i>		
1	—	0.070	0.08	—	6.6	7.67	—	0.46	0.61	—	1.3
2	0.245	0.180	5.82	166.9	15.5	2.27	40.9	2.79	13.21	0.093	4.7
3	0.203	0.125	6.26	270.3	14.5	1.49	54.9	1.82	9.33	0.054	5.1
4	0.196	0.115	6.74	220.5	11.9	1.35	39.3	1.37	9.10	0.057	6.6
5	0.158	0.097	6.73	372.7	12.7	1.07	58.9	1.23	7.20	0.034	5.9
Coke <sup>b</sup>	—	—	—	13.06	—	—	—	—	—	—	—

<sup>a</sup> Each slug contained 6.86 cc(NTP) of *cis*-2-butene with about 0.1% 1-C<sup>14</sup>-butene-1; 0.60 g of catalyst having a surface area of 143 m<sup>2</sup>/g was used; the carrier gas flow rate was 28 cc(NTP) min<sup>-1</sup>. The specific activity of the starting mixture was 10.9 × 10<sup>4</sup> c min<sup>-1</sup> cc<sup>-1</sup> (based on total gas).

<sup>b</sup> Coke burned off catalyst expressed as equivalent cc butene.

mixtures of 1-butene and *cis*-2-butene, with either one or the other radioactive, were alternately passed over the catalyst, trapped, and again analyzed for radioactivity. Finally, the M-3 procedure included passage of identical size slugs containing pure 1-butene or pure *cis*-2-butene over the catalysts. The product ratio, at low conversion, was taken to be the selectivity.

**Survey procedure.** The four-part survey procedure (labeled S-1, S-2, C-3, and S-4) combined both microcatalytic and steady state flow experiments. Each sample (~1.0 g) of alumina containing varying amounts of fluorine was treated in the following way: (S-1) approximately 15 3.1-cc (NTP) slugs of 1-butene were passed in succession over the catalyst in the microcatalytic equipment described above; (S-2) a continuous stream containing 45% 1-butene and 55% helium was then allowed to flow over the same catalyst at 58 cc (NTP)/min and 1 atm pressure while repeated analyses of the effluent gas were made as the reactor was cycled over six different temperatures; (S-3) Part S-1 was repeated on the "poisoned" catalysts; and (S-4) the catalysts were regenerated by a standard pretreatment (*vide infra*) and again subjected to Part S-1. These experiments, and the conditions used, agree in detail with those reported earlier (16) for the unfluorinated parent alumina.

**C<sup>14</sup> analysis.** For radioactivity determinations the *n*-butene samples were each ex-

panded into a 30-cc vacuum-tight system separated by a thin mica window from an open-end Kummer-type Geiger counter (22). Counts were recorded on a Tracerlab Superscaler, and the specific activity for each sample was given as counts min<sup>-1</sup> mm<sup>-1</sup> [or counts min<sup>-1</sup> cc(NTP)<sup>-1</sup>] of butene, the pressure being read on a mercury manometer with a traveling cathetometer. Metal Hoke valves were used to isolate the counting system; this prevented cross contamination of radioactive samples via stop-cock grease. Although the efficiency of the counter was quite low (~5%), the total activity of the tracers used was such that measurements in most cases were reproducible to well within ±5%.

**Catalysts.** The GA-48 alumina (23-25), which was made by the neutral hydrolysis of redistilled aluminum isopropoxide, was furnished by the MK Research & Development Co., Pittsburgh, Pennsylvania. The total metallic impurity level was less than 50 ppm. Catalyst particles were sieved to 20-40 mesh with a surface area of 158 m<sup>2</sup>/g and X-ray measurements, made as the catalyst was dehydrated during the final stages of its preparation, indicated that it was probably a mixture of eta and gamma alumina. The WRG-A alumina was prepared by dehydration (evacuation at 550°C) of beta aluminum trihydrate kindly furnished by W. R. Grace & Co.; its surface area was 250 m<sup>2</sup>/g.

MSA-3-H (Houdry M-46, 13% alumina,

270 m<sup>2</sup>/g, 20–40 mesh), WRG-SA (W. R. Grace, 13% alumina, Series B reference catalyst, 556 m<sup>2</sup>/g, particles smaller than 70 mesh) and AAA-SA (American Cyanamid Aerocat high alumina, 430 m<sup>2</sup>/g, particles smaller than 70 mesh) were all commercial silica-alumina catalysts.

The fluorided aluminas (FA-%) were prepared from GA-48 and contained from 0 to 6 wt % fluorine. The methods of their preparation, determination of hydroxyl contents, and measurements of ammonia chemisorption capacities have been described elsewhere (24).

In all cases the catalyst particles would pass a 20-mesh sieve. Duplicate experiments using 20- to 40-mesh and  $\leq$  70-mesh particles of GA-48 showed the same overall activity and selectivity. The similarity of the relative rate constants, determined over catalysts whose particle diameters varied widely, indicated that diffusion was not disguising the kinetics.

**Catalyst pretreatment.** Before use, the catalysts were all given a standard pretreatment which included burning in a stream of dry oxygen at 550°C for 2 to 3 hr followed by a 15-hr evacuation at the same temperature to pressures less than 10<sup>-5</sup> torr. Since the pure alumina catalysts did not poison appreciably, rate measurements were made on fresh samples. The fluorided aluminas and silica-aluminas, on the other hand, all formed considerable residue or "coke," and several slugs were required before the activity lined out; it was on these "poisoned" catalysts that the relative rate measurements were made.

**Reactants.** In the microcatalytic experiments, all the *n*-butenes (Phillips Research Grade) were distilled from -78 to -195°C and outgassed. In the tail-gas experiments, the 1-butene (Phillips Pure Grade) was passed over sodium hydride and Drierite. GLC indicated less than 0.5% impurity in each of the gases; butadiene was not detected.

The 1-butene, 1-C<sup>14</sup> (4.2 mc/mM) was purchased from Tracerlab and was used without dilution following purification by gas chromatography. *cis*-2-Butene, 1-C<sup>14</sup> was prepared from the radioactive 1-butene by

isomerization over a small sample of the FA-1.2 which gave a high *cis/trans* product ratio. In the prepared mixtures, the radioactive material represented less than 0.2% of the total butenes.

Between slugs containing different radioactive compounds, the entire gas-handling system was thoroughly flushed with non-radioactive 1-butene to remove any traces of radioactivity which could have been retained in stopcock grease. Frequent tests following this treatment demonstrated that all the radioactive material had been removed.

## RESULTS

### *Microcatalytic Experiments*

Table 1 details the results of a typical experiment. Were the *cis* isomerized to the *trans* isomer via intermediate 1-butene, as indicated by Eq. (3), the specific activity of *trans*-2-butene should equal, or exceed, that of 1-butene. This was not the case (next to last column), nor did the specific activity of the *trans* equal or exceed that of the *cis* isomer when 1-butene, containing a trace of *cis*-2-butene-C<sup>14</sup>, was isomerized. What actually occurred was that the radioactive trace component reacted with the same selectivity it would have had were it the only reactant. The Total Activity of the product was obtained by multiplying the quantity of gas by its specific activity; this measures the amount of the tracer which has been converted to a particular compound. Thus, the Ratio of Total Activities (last column) indicates a *cis/trans* ratio of about 5 for 1-butene over this catalyst, in agreement with earlier work (16). It is of particular interest that radioactive 1-butene literally "swims upstream" against the strong current of isomerizing *cis*-2-butene.

The relative rate constants for the six *n*-butene interconversion reactions as determined by the three microcatalytic techniques are given in Table 2. Calculations for the M-1 procedure were made in the following way: If the starting mixture were 1-butene with a trace of C<sup>14</sup> *cis*-2-butene, at low conversions the ratio  $k_{1c}/k_{1t}$  was

TABLE 2  
RELATIVE RATE CONSTANTS FOR *n*-BUTENE INTERCONVERSION REACTIONS OVER ALUMINA,  
FLUORIDED ALUMINA, AND SILICA-ALUMINA

Expt. No.	Catalyst	Temp. (°C)	Method	Relative rate constants, $k/k_{1c}$									Residue [(Molecule/cm <sup>3</sup> ) × 10 <sup>-14</sup> ]
				$k_{1c}$	$k_{c1}$	$k_{t1}^a$	$k_{1t}$	$k_{ct}$	$k_{tc}^a$	$k_{1c}/k_{1t}$	$k_{c1}/k_{ct}$	$k_{t1}/k_{tc}$	
1	MSA-3-H	50	M-1 <sup>b</sup>	1.0	0.21	0.05	0.91	0.29	0.09	1.10	0.73	0.56	0.8
2	MSA-3-H	50	M-1 <sup>c</sup>	1.0	0.21	0.06	0.95	0.31	0.09	1.05	0.68	0.67	0.8
3	MSA-3-H	50	M-2	1.0	0.24	0.06	1.00	0.34	0.10	1.00	0.71	0.60	—
4	MSA-3-H	50	M-3	1.0	0.27	0.06	1.04	0.46	0.14	0.96	0.59	0.43	—
5	AAA-SA	24	M-3	1.0	0.15	0.04	0.91	0.28	0.07	1.10	0.54	0.57	—
6	WRG-SA	24	M-3	1.0	0.15	0.05	1.00	0.26	0.07	1.00	0.58	0.72	—
7	GA-48	50	M-1 <sup>b</sup>	1.0	0.21	0.03	0.45	0.91	0.25	2.21	0.23	0.12	0.1
8	GA-48	50	M-1 <sup>c</sup>	1.0	0.21	0.03	0.54	1.05	0.31	1.84	0.20	0.10	0.1
9	GA-48	49	M-2	1.0	0.21	0.03	0.49	1.11	0.33	2.04	0.20	0.09	—
10	GA-48	49	M-3	1.0	0.21	0.03	0.49	0.87	0.24	2.05	0.24	0.13	—
11	WRG-A	24	M-3	1.0	0.15	0.03	0.59	0.75	0.20	1.69	0.20	0.15	—
12	FA-0.1	63	M-2	1.0	0.29	0.04	0.72	1.67	0.53	1.39	0.17	0.08	—
13	FA-0.1	63	M-3	1.0	0.23	0.04	0.77	1.20	0.39	1.30	0.19	0.10	—
14	FA-0.5	89	M-2	1.0	0.30	0.03	0.31	0.45	0.16	3.23	0.67	0.19	—
15	FA-0.5	89	M-3	1.0	0.20	0.02	0.24	0.40	0.15	4.16	0.50	0.13	—
16	FA-1.2	51	M-1 <sup>b</sup>	1.0	0.21	0.01	0.19	0.12	0.03	5.20	1.71	0.33	1.7
17	FA-1.2	86	M-2	1.0	0.30	0.02	0.21	0.15	0.05	4.76	2.00	0.40	—
18	FA-1.2	86	M-3	1.0	0.21	0.02	0.22	0.13	0.05	4.55	1.62	0.40	—
19	FA-5.2	71	M-2	1.0	0.26	0.04	0.49	0.24	0.08	2.04	1.08	0.50	—
20	FA-5.2	71	M-3	1.0	0.22	0.03	0.40	0.20	0.07	2.50	1.10	0.43	—
Equilibrium <sup>a</sup>		50	—	1.0	0.21	0.21	3.35	3.44	1.02	0.30	0.06	0.21	—
Equilibrium <sup>a</sup>		88	—	1.0	0.25	0.25	2.81	2.78	0.97	0.36	0.09	0.25	—

<sup>a</sup> Calculated from thermodynamic equilibrium constants (27).

<sup>b</sup> *cis*-2-Butene with a trace of C<sup>14</sup>-1-butene.

<sup>c</sup> 1-Butene with a trace of C<sup>14</sup>-*cis*-2-butene.

determined directly from the gas chromatographic analysis of the *cis*-/*trans*-2-butene ratio. In the same experiment, the ratio  $k_{c1}/k_{ct}$  was calculated from the total amounts of radioactive material which appeared in the 1-butene and the *trans*-2-butene. Assuming the ratios  $k_{1c}/k_{c1}$ ,  $k_{1t}/k_{t1}$ , and  $k_{ct}/k_{tc}$  are defined by the thermodynamic equilibrium constants  $K_{eq}$ , all six relative rate constants ( $k_{1c}$  taken arbitrarily as unity) were obtained. The same calculations were involved when the starting mixture was *cis*-2-butene containing a trace of C<sup>14</sup> 1-butene.

In the M-2 experiments, the partial pressures of both 1-butene and *cis*-2-butene were the same. If the 1-butene were radioactive, the relative amounts of radioactivity which appeared in the *cis*- and *trans*-2-butenes determined the ratio

$k_{1c}/k_{1t}$ . From the dilution of the 1-butene specific activity, one could also calculate the amount of nonradioactive material which passed from *cis*-2-butene into 1-butene and hence demonstrate that the ratio  $k_{1c}/k_{c1}$  was equal to the thermodynamic equilibrium constant between the two isomers. By alternately passing over the catalysts 1:1 mixtures of *cis*-2-butene and 1-butene where first one and then the other was radioactive, very precise relative measurements could be obtained for  $k_{1c}$ ,  $k_{c1}$ ,  $k_{1t}$ , and  $k_{ct}$ . Both  $k_{t1}$  and  $k_{tc}$  were calculated from the rate constants for the reverse reactions,  $k_{1t}$  and  $k_{ct}$ , and their corresponding equilibrium constants.

Ratios of  $k_{1c}/k_{1t}$  and  $k_{c1}/k_{ct}$  were obtained in the M-3 procedure simply from the low conversion product ratios when identical size slugs of 1-butene and *cis*-2-

butene were alternately passed over the catalysts. The ratios  $k_{c1}/k_{1c}$  given in Table 2, Col. 6 ( $k_{1c} \equiv 1$ ) were experimentally determined from the relative amounts of 1-butene from *cis*-2-butene, and *cis*-2-butene from 1-butene, when the two isomers were passed in succession over each catalyst under identical conditions.

A cursory examination of the data in Table 2 will show that the three microcatalytic procedures yielded similar results. All three commercial silica-alumina catalysts exhibited comparable selectivities, but these differed substantially from those obtained with either the alumina or the fluorided alumina samples.

Over silica-alumina, the initial ratio of the products formed from any one of the *n*-butenes was unity ( $\pm 0.5$ ). Whenever there was a choice between *cis*-*trans* or double-bond isomerization (e.g., in reaction of either 2-butene), the latter always occurred preferentially, when compared with thermodynamic equilibrium of the two products. The *cis*-2-butene was also formed in above equilibrium amounts with respect to the more stable *trans* isomer from 1-butene, but most of the *trans*-2-butene in the initial product was formed directly from 1-butene. 1-Butene reacted about four times as rapidly as did *cis*-2-butene as can be seen from the ratio of the rate constant

sums  $(k_{1c} + k_{1t})/(k_{c1} + k_{ct})$ . Temperature apparently had little effect on the selectivity.

Over the alumina catalysts, the least-favored reaction paths are between 1-butene, and *trans*-2-butene, and the most-favored ones lie between 1-butene and *cis*-2-butene and between *cis*- and *trans*-2-butene. This resulted in high *cis/trans*, *cis*/1-butene and low 1-butene/*trans* ratios. Thus, most of the *trans*-2-butene in the product was formed from *cis*-2-butene, even when 1-butene was the reactant. Both *cis*-2-butene and 1-butene reacted at similar rates, the ratio  $(k_{1c} + k_{1t})/(k_{c1} + k_{ct})$  averaging about 1.2.

The relative rate constants, and hence the selectivity, changed considerably as fluorine was added to alumina (Table 2); the overall activity changed relatively little (Table 3). The ratios  $k_{1c}/k_{1t}$  and  $k_{c1}/k_{ct}$  were always above equilibrium and passed through maxima near 1% F.

A final observation concerns the "residue" which was deposited on the catalysts. The residue was defined as that amount of material which was not desorbed from the catalyst after 30 min in a stream of helium at reaction temperature. In most cases, the residue was deposited from the first slug with very little material being lost from the second and subsequent slugs. The last

TABLE 3  
RESULTS FROM 1-BUTENE TAIL GAS EXPERIMENTS OVER SOME FLUORIDED ALUMINA CATALYSTS

Catalyst	Surface area (m <sup>2</sup> /g)	Flow expts. <sup>a</sup> after 40 hr at 175°C—Part S-2			Slug expts. at 50°C <sup>b</sup>				Hydrogen or halide content $\times 10^{-14}$	
		$E_{act}$ (kcal/mole)	$kK \times 10^{-8}$ (mole atm sec <sup>-1</sup> m <sup>-2</sup> )	Initial ratio <i>cis/trans</i>	$kK \times 10^{-8}$ (mole atm sec <sup>-1</sup> m <sup>-2</sup> )			Residue <sup>c</sup> [(molecules/cm <sup>2</sup> ) $\times 10^{-14}$ ]	OH/cm <sup>2</sup>	F/cm <sup>2</sup>
					S-1	S-3	S-4			
Control-0	143	17	12.3	0.6	7.7	0.6	10.2	0.1	2.6	0.0
Control-0	152	16	7.9	0.6	—	—	—	—	—	—
Control-0	152	20	7.0	0.6	—	—	—	—	—	—
FA-0.1	150	14	4.7	1.7	5.6	0.3	6.9	0.5	2.6	0.2
FA-0.5	139	19	2.0	3.7	3.9	—	3.8	1.5	2.1	1.1
FA-1.2	136	17	3.7	5.1	4.1	0.2	6.3	2.5	1.4	2.8
FA-1.7	137	16	4.7	4.8	4.8	0.4	4.5	2.1	1.0	4.0
FA-2.7	133	14	4.7	5.3	5.2	0.7	4.3	1.6	0.77	6.5
FA-5.2	122	13	6.5	3.1	6.0	0.4	4.3	0.9	0.08	13.5

<sup>a</sup> Flow rate was 58 cc(NTP)/min of 45% 1-butene, 55% He at 1 atm.

<sup>b</sup> Flow rate was 28 cc(NTP)/min at  $\sim 2$  atm. Slug size was 3.1 cc(NTP). Data from fifth slug.

<sup>c</sup> Each slug contained 0.5 to  $0.7 \times 10^{14}$  molecules/cm<sup>2</sup>.

column in Table 2 gives the residue in terms of butene molecules/cm<sup>2</sup> of catalyst surface. Pure alumina retained only a small amount of butene (less than 0.1 butene molecule/surface OH group) (24), and analysis of radioactivity in a blank slug which followed one containing radioactive material indicated that most of the residue was displaced by the second slug. Very little poisoning was observed with the alumina catalyst. Just the opposite was true with fluorided alumina and silica-alumina. Relatively large amounts of residue were deposited from the first slug, and the catalytic activity dropped by over an order of magnitude from the first to the second slug. The number of butene molecules lost to the silica-alumina ( $0.8 \times 10^{14}$ /cm<sup>2</sup>) is fairly close to the number of surface hydroxyl groups ( $1.4 \times 10^{14}$ /cm<sup>2</sup>) (24) present on the catalyst. By successive passage of radioactive and nonradioactive reactants over silica-alumina, it was found that less than 2% of the residue could be displaced by the following slug. There appeared to be no correlation between the residue and either the fluorine or hydroxyl content of the fluorided alumina catalysts (Table 3).

Over both silica-alumina and fluorided alumina the residue was apparently formed more readily from 1-butene than from either 2-butene isomer. When mixture M-1<sup>b</sup> (1-butene radioactive) was passed over either catalyst, the burned off residue had a higher specific activity (from 1.2 to 2.0 times higher) than did the starting mixture (see Table 1). Conversely, from mixture M-1<sup>c</sup> (*cis*-2-butene radioactive), the recovered residue had a specific activity somewhat lower than that of the starting mixture.

#### Tail Gas Experiments

Results obtained from the 1-butene "tail gas" experiments over fluorided aluminas are summarized in Table 3. The effective rate constants  $kK$  ( $k$  is the first order rate constant and  $K$  is the adsorption equilibrium constant) were based on a relationship derived by Bassett and Habgood (26),

$$kK = -(F^0/273RW) \ln(1 - X) \quad (4),$$

and used in an earlier paper (16). The equation was modified to correct for back reaction and normalized to unit surface area rather than weight. Its final form was

$$kK = -(F^0 X_e / 273RS) \ln(1 - X/X_e) \quad (5),$$

where  $F^0$  was the flow rate in cc(NTP)/min,  $R$  the gas constant,  $S$  the surface area in cm<sup>2</sup>,  $X$  the mole fraction converted, and  $X_e$  the mole fraction of 2-butene at equilibrium.

The first order character of the reaction was confirmed in a flow experiment over the 1.2% fluorided alumina in which the flow rate was changed at constant temperature. When  $1/F^0$  was plotted against

$$\log\left(\frac{1}{1 - X/X_e}\right),$$

a straight line resulted (Fig. 1). Similar results were reported earlier (16) for alumina and silica-alumina catalysts.

Because most of the first slug and significant parts of slugs 2-4 were irreversibly adsorbed on the fresh catalysts as residue (see col. 9, Table 3), the values of  $kK$  in S-1 and S-4 were calculated from results obtained with the fifth slug and did not represent the intrinsic activity of the catalysts. After the catalysts had been "poisoned" in flowing 1-butene for 40 hr, the  $kK$  values (S-3) were an order of magnitude smaller than those on the fresh samples. However, the original activity of the poisoned catalysts could be restored by subjecting them to a standard pretreatment (compare S-1 and S-4).

In the flow experiments, neither the activation energy (about 16 kcal/mole) nor the absolute activity were appreciably affected by the addition of fluorine. However, as was observed with similar catalysts in the microcatalytic experiments, the selectivity (*cis/trans* ratio extrapolated to zero conversion) increased to a maximum, then decreased as the fluorine content increased. These data are compared with those from the microcatalytic experiments in Fig. 2. A similar maximum was also observed in the amount of residue which

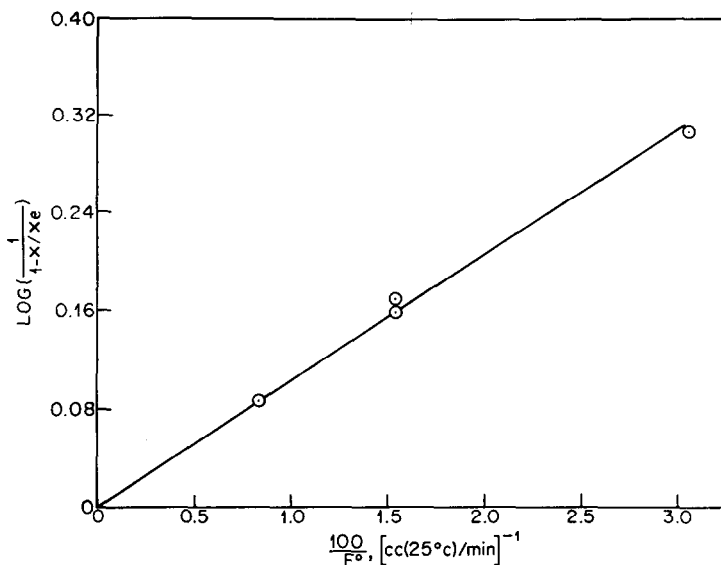


FIG. 1. First order dependence of 1-butene isomerization over FA-1.2% at 171°C.

was deposited on these fluorided aluminas (Fig. 2).

#### DISCUSSION

All the relative rate constants given in Table 2 are based on first order kinetics, and three experimental facts lend support to the validity of this assumption. (1) None of the selectivities was pressure-dependent; in the M-1 experiments similar selectivities resulted from 1-butene and *cis*-2-butene regardless of whether the compound was the major nonradioactive component or the radioactive tracer, the pressure of which was about three orders of magnitude lower. Similar results were obtained when the partial pressures of the two reactants were equal, as in the M-2 experiments (for example, compare 1, 2, and 3, or 7, 8, and 9 in Table 2). (2) The ratio of the amount of 1-butene formed from *cis*-2-butene to the amount of *cis*-2-butene formed from 1-butene ( $k_{c1}/k_{1c}$ ) was approximately equal to the thermodynamic equilibrium constant when the two pure compounds were alternately passed at the same pressure over the catalysts in M-3. Items (1) and (2) demonstrate that all of the elementary reactions have the same *simple* pressure dependence, i.e.,  $r_{ij} = k_{ij}p^n$ . (3) Finally, the straight

line in Fig. 1 shows that the reaction follows Eq. (4), demonstrating that  $n = 1$ . Other investigators (3, 7, 11) have also suggested that the *n*-butene reactions are first order over similar catalysts.

The selectivities (e.g., initial *cis/trans* ratios) did not appear to be greatly affected by either the temperature, the degree of poisoning or the method of determination. In Fig. 2 the *cis/trans* ratios obtained by the microcatalytic technique at 63–86°C are similar to those obtained in the flow experiments at 171°C for a given catalyst composition. Similar results were reported earlier (16) for alumina and silica-alumina.

Brouwer (11) found that the selectivity of a gamma-alumina catalyst changed greatly with time when subjected to a stream of *cis*-2-butene, but such a change in selectivity was not observed in our microcatalytic experiments over alumina. Perhaps traces of butadiene (as he suggested), CO<sub>2</sub>, or some other poison were responsible for the changes he observed.

A detailed discussion of the reaction mechanisms over alumina and silica-alumina will be given in a later paper, but the relative rate constants listed herein can be used to test some of the mechanisms currently in the literature, with the reserva-



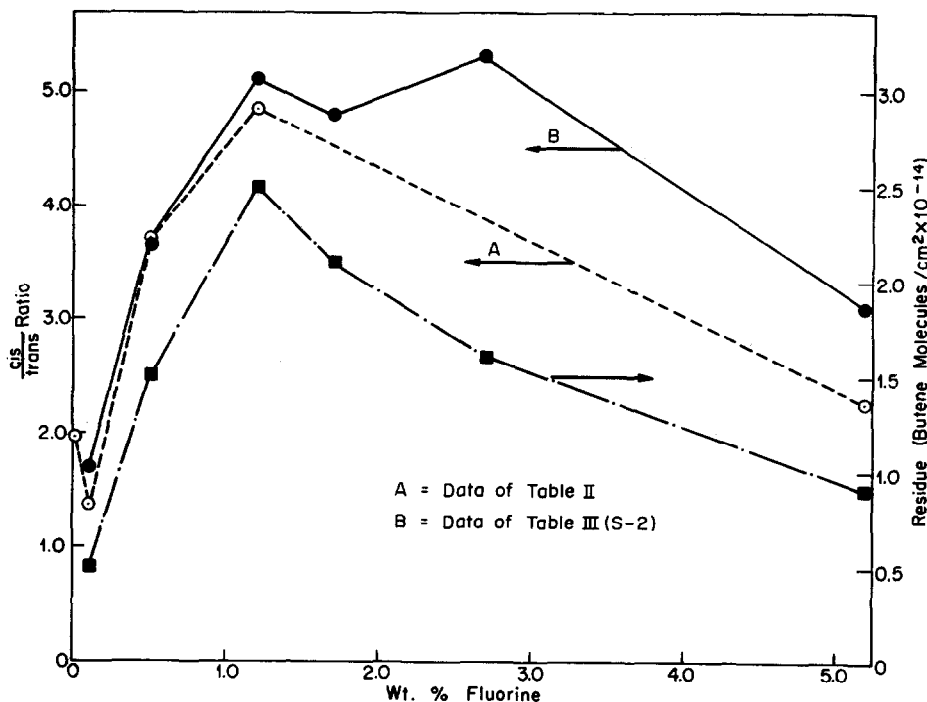


FIG. 2. Changes in *cis/trans* ratio and residue formation as fluorine is added to alumina: A, data of Table 2; B, data of Table 3 (S-2).

tion noted in the Introduction, viz., that the surface reaction is rate-limiting. The allylic carbonium ion postulated by Leftin and Hermana (15) and the fixed-configuration nonclassical carbonium ion advanced by Lucchesi *et al.* (6) to explain *n*-butene isomerization over silica-alumina share common features. Both mechanisms suggest that one of the *n*-butenes is formed from another only through the third as an intermediate, i.e., one of the reaction paths interconnecting the three isomers is excluded [see Eqs. (2) and (3)]. Both assumed (as we do) that the surface reaction controls the kinetics. The results reported herein indicate that all reaction paths exist. In fact, the selectivities from each of the three isomers is not far from unity, i.e., every isomer is formed from another as a primary product. Brouwer (11) has obtained similar results over partially deactivated silica-aluminas and has drawn similar conclusions. Hence, the above-mentioned mechanisms, if operative, must have others superimposed. For example, *cis*-2-butene is

converted directly to the *trans* isomer over silica-alumina. If the allylic carbonium ion is responsible for double-bond isomerization, as suggested by Leftin and Hermana (15), then *cis-trans* isomerization must also be occurring on a different set of sites. Since the allylic ion was invoked partly to explain the selectivity, this mechanism loses much of its appeal. The same applies to the concerted hydrogen-switch mechanism of Turkevich and Smith (2), which provides only for double-bond isomerization. *Cis-trans* isomerization must then occur elsewhere on the same surface rather than via intermediate 1-butene [Eq. (1)].

Our results are not inconsistent with the classical secondary carbonium ion intermediate often postulated to explain *n*-butene isomerization over silica-alumina. If the 2-butyl carbonium ion were formed from all isomers, it would not be surprising to find product ratios near unity for all reactants. This was suggested by simple statistical arguments (16). Also consistent, the selectivities were not appreciably

affected either by added-back water (which increased the activity) or by such poisons as alkali or coke. It was shown earlier (16) that the isomerization rates correlated with catalyst hydrogen content, although it was found (18) that only a small fraction of the surface hydroxyl groups can be directly involved as sites for *n*-butene isomerization reactions. However, protons for carbonium ion formation may be provided by residue. It is probable that the spectroscopic studies of both Leftin and Hermana (15) and of Peri (14) were made of this residue. These possibilities will be considered in detail in future papers in this series.

The situation was quite different over alumina, where the isomerization rates actually correlated inversely with catalyst hydrogen content (11, 16). The changes in selectivity which resulted from addition of water, fluorine, or "poisons" strongly suggest that a common intermediate may not be involved in all reaction paths. The only intermediate which has been considered which provides direct pathways between all three isomers is the 2-butyl carbonium ion. If this ion is responsible for the results obtained with silica-alumina, it cannot, by classical concepts, account for the much different selectivities found for alumina. It therefore appears that several reactions are occurring simultaneously on the same surface. These may involve different sites or different intermediates.

Aluminas which have been exchanged with fluoride ions possess some of the characteristics of both alumina and silica-alumina. Like silica-alumina, they retained large amounts of residue and were subject to very rapid initial poisoning, but like alumina their selectivities were quite different from either thermodynamic equilibrium or unity. The addition of fluoride ions to alumina decreased the hydroxyl content (24) and altered the acidity, but this apparently had little effect on the steady state activity in the tail gas experiments. Disappointingly, it has not been possible to rationalize satisfactorily the rather complicated changes in selectivity which occurred as alumina was fluorided in terms of the chemistry of these surfaces. The maxi-

mum in selectivity (Fig. 2) correlated with the amount of residue held by the catalyst and appeared to stem from an enhancement of the rates between 1-butene and *cis*-2-butene, relative to those connecting these compounds to *trans*-2-butene. It seems likely that these results reflect the simultaneous operation of several mechanisms.

#### ACKNOWLEDGMENTS

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum. Thanks are due Mr. Fred M. Allen for capable assistance with the experiments.

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