

## Kinetic Study of 1-Butene Isomerization on Alumina at 510–550°C

L. FORNI, L. ZANDERIGHI, AND S. CARRÀ

*From the Istituto di Chimica Fisica Università, Milano, Italy*

Received July 30 1968; revised August 22, 1968

A kinetic study of 1-butene isomerization on nonactivated alumina at 510°, 530°, and 550°C has been performed in a flow system. The kinetic runs were made by feeding mixtures of 1-butene and nitrogen or 1-butene, nitrogen, and ammonia at various partial pressures. The results, interpreted in the Langmuir-Hinshelwood scheme, confirmed the existence of a thermal activation of the catalyst. The presence of ammonia decreases the reaction rate consistently with a competitive adsorption of this gas on the isomerization active centers.

### INTRODUCTION

Recent studies (1, 2, 3) with respect to the mechanism of the isomerization of 1-butene on alumina revealed the importance of the effect of thermal activation of the catalyst on the reaction.

This fact has been related to the possibility that active centers of isomerization are exposed pairs of aluminum ions, the surface concentration of which increases with increasing temperature. This interpretation involves the fact that adsorption equilibria of olefins on alumina are affected by the equilibrium of active center formation on the catalyst surface. This corresponds to the fact that at higher temperatures a greater number of adsorption centers are present.

In the present paper some results of a kinetic analysis of 1-butene isomerization at high temperatures (510–550°C) are reported, with the purpose of testing the influence of adsorption status on the reaction kinetics. Therefore some runs in a flow system at various partial pressures of the olefin were made with the aim of evaluating by a kinetic analysis the constants both of the reaction rate and of adsorption equilibrium of 1-butene.

Alumina not thermally activated has been employed as a catalyst; its activation took place under the reaction conditions during the first stage of the reaction, before the collection of kinetic samples. A set of runs

performed in the presence of ammonia allowed establishment of the effect on the reaction kinetics of the presence of such a gas, and so to what extent its adsorption competes with olefin adsorption.

### EXPERIMENTAL

**Materials.** 1-Butene was a "pure grade" Phillips Petroleum Co. product. Its purity, tested by gas chromatography, was > 99.5%, the remaining part being *n*-butane with traces of propane and propylene. Ammonia had a purity of > 99.99%; nitrogen > 99.999%.

The alumina was an Alcoa F-110 product, the major properties of which were the following: Na<sub>2</sub>O; 0.08%; surface area; 180–280 m<sup>2</sup>/g; internal porosity; 0.272. The product was crushed and sieved: sizes between 20 and 40 mesh were collected.

**Equipment.** The dehydrogenation runs were performed in a stainless steel (type 446) reactor, previously described (4). 1-Butene, nitrogen, and ammonia, taken from cylinders and metered by calibrated rotameters, were mixed and fed to the reactor. After reaction the outcoming gas was cooled by means of a double pipe heat exchanger and, by a suitable system of valves, it could be sent to a soap bubble flow meter or to a sample collector. The temperatures of the metered gases were taken by mercury thermometers inserted in the gas pipes. The flow

diagram of the apparatus is given in the previous paper (4).

**Procedure.** All runs were conducted with fresh catalyst as follows: After the weighed quantity of catalyst had been introduced into the catalyst basket, the reactor was stopped and flushed with a small nitrogen flow (50 ml/min) to eliminate oxygen. During this flushing the reactor temperature was raised up to 100°C below the chosen reaction temperature and at this point we started the feeding of the gas mixtures at the desired flow rates and ratios. One hour after starting the feeding of the reacting gases the first sample of reacted gases was taken, controlling and recording all experimental conditions and data (temperatures, flow rates, etc.).

The second and the third samples were collected after 1.5 and 2 hr respectively, and in the same way as the first one.

**Analysis.** The analysis of the gases entering and leaving the reactor was performed by gas chromatography, employing a Fractovap mod. B/f C. Erba thermal conductivity detector gas chromatograph. Satisfactory results have been obtained with a copper column, 4-mm ID and 8 m long, packed with 60–100 mesh activated alumina impregnated with propylene carbonate (21% by weight), which has been operated at the following conditions: column temperature 15°C; carrier gas hydrogen 10–30 ml/min; injected samples 3 ml.

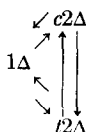
## RESULTS

A set of runs were performed at 510°, 530°, and 550°C at different 1-butene partial pressures and the results are collected in Table 1.

A second set of runs were made by feeding a mixture of 1-butene at different partial pressures of ammonia. The results are shown in Fig. 6.

### Kinetic analysis

The general scheme of the 1-butene isomerization reaction is the following:



Where 1 $\Delta$  represents 1-butene; and  $c2\Delta$  and  $t2\Delta$ , *cis*- and *trans*-2-butene.

The amount of the dehydrogenation reaction under our conditions did not exceed 2% (Table 1, column  $X_4 = \Delta\Delta$ ) and therefore the kinetic analysis of isomerization has been performed neglecting this reaction.

Some runs, held for a period of several hours at 550°C, showed that the deactivation of the catalyst during the reaction time (about 2 hr) was also negligible. The kinetic equations of the isomerization reaction may then be written as follows:

$$-dx_1/d\tau = r_{12} + r_{13} - r_{21} - r_{31} \quad (1a)$$

$$-dx_2/d\tau = r_{21} + r_{23} - r_{12} - r_{32} \quad (1b)$$

$$-dx_3/d\tau = r_{31} + r_{32} - r_{13} - r_{23} \quad (1c)$$

where  $x_1, x_2, x_3$  are, respectively, the mole fractions of 1-butene, *trans*-2-butene and *cis*-2-butene, referred to the olefin feed;  $r_{ij}$  indicates the reaction rate of transformation of the  $i$ th component to the  $j$ th one;  $\tau$  is the contact time, defined as  $\tau = W/F$ ,  $W$  being the weight of catalyst in grams and  $F$ , the moles/hr of 1-butene in the feed.

Assuming that the rate-determining step is a surface reaction and that the adsorption equilibrium constants have the same value for the three isomers, in the Langmuir-Hinshelwood scheme  $r_{ij}$  may be written as

$$r_{ij} = k_{ij} \frac{b_{\Delta} P_i}{1 + b_{\Delta} P_{\Delta}} = k_{ij} \frac{b_{\Delta} P_{\Delta} x_i}{1 + b_{\Delta} P_{\Delta}} \quad (2)$$

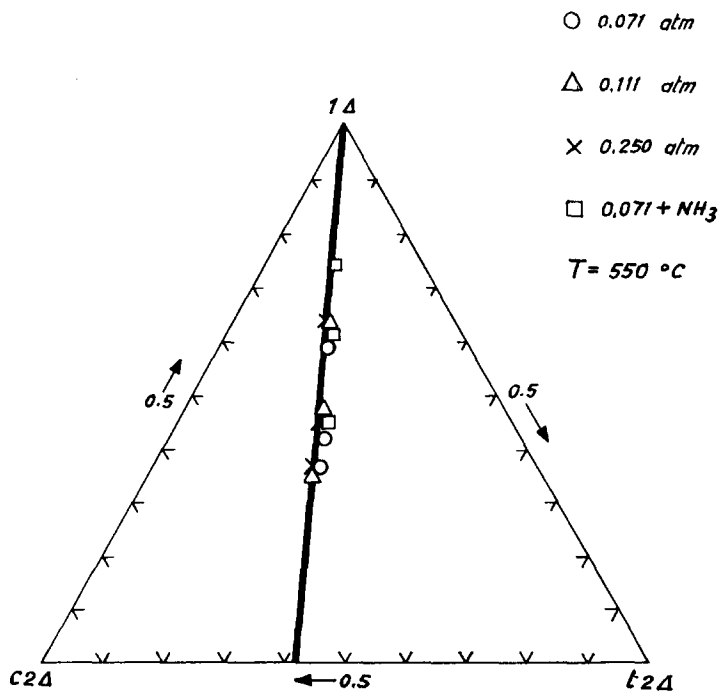
where  $r_{ij}$  is the reaction rate (reacted moles/hr g cat.);  $k_{ij}$ , the reaction rate constant (moles/hr g cat.);  $P_i$ , the partial pressure of the reagent  $i$  (atm);  $P_{\Delta}$ , the partial pressure of 1-butene in the feed (atm); and  $b_{\Delta}$ , the adsorption equilibrium constant (assumed the same for the three butenes) ( $\text{atm}^{-1}$ ).

The reaction paths in triangular diagrams have been made for all the temperatures and an example is shown in Fig. 1. On the same diagram the equilibrium composition of the *cis*-*trans*-2-butene system (solid line) taken from literature data (5) is also drawn.

One can see that our experimental data lie on that line independently from contact time and from 1-butene partial pressure in the feed, so that we can correctly assume that under our conditions the *cis*-*trans*-2-butene system is always at equilibrium.

TABLE 1  
 RUNS PERFORMED IN THE ABSENCE OF AMMONIA

$T$ (°C)	$P_{\Delta}$ (atm)	$\tau = W/F$ (hr/mole g cat.)	$x_1 = 1\Delta$	$x_2 = t2\Delta$	$x_3 = c2\Delta$	$x_4 = \Delta\Delta$
510°	0.071	2.73	0.670	0.181	0.147	0.001
510°	0.071	5.49	0.500	0.277	0.220	0.003
510°	0.071	10.90	0.377	0.352	0.266	0.004
510°	0.111	2.38	0.647	0.202	0.149	0.002
510°	0.111	3.39	0.564	0.253	0.181	0.002
510°	0.111	6.68	0.433	0.328	0.235	0.004
510°	0.250	1.20	0.692	0.180	0.126	0.001
510°	0.250	2.39	0.548	0.262	0.188	0.001
510°	0.250	4.74	0.418	0.343	0.235	0.003
530°	0.071	2.72	0.631	0.204	0.162	0.002
530°	0.071	5.47	0.471	0.293	0.231	0.004
530°	0.071	10.90	0.372	0.346	0.275	0.007
530°	0.111	1.93	0.637	0.208	0.152	0.003
530°	0.111	3.34	0.568	0.245	0.184	0.004
530°	0.111	6.65	0.474	0.299	0.221	0.005
550°	0.071	2.64	0.590	0.230	0.174	0.006
550°	0.071	5.30	0.423	0.324	0.242	0.011
550°	0.071	10.87	0.352	0.363	0.270	0.016
550°	0.111	1.73	0.634	0.201	0.161	0.004
550°	0.111	3.33	0.480	0.293	0.219	0.007
550°	0.111	6.65	0.345	0.377	0.282	0.013
550°	0.250	1.22	0.647	0.200	0.148	0.004
550°	0.250	2.39	0.469	0.302	0.222	0.007
550°	0.250	4.61	0.384	0.354	0.251	0.011


 FIG. 1. Reaction paths of 1-butene isomerization at 550°C and various partial pressures. Solid line represents the equilibrium composition of *cis/trans*-2-butenes.

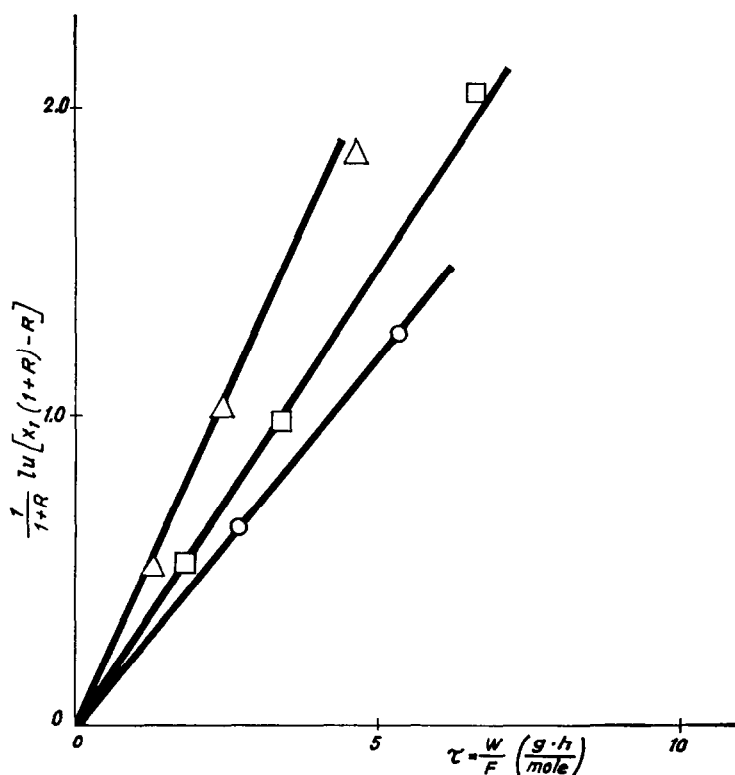


Fig. 2. Linear plots of Eq. (8):  $\circ$ , 510°C;  $\square$ , 530°C;  $\triangle$ , 550°C.

Therefore Eq. (1a) is sufficient to completely represent the reaction path of our system. Putting Eq. (2) into Eq. (1a) we have

$$-\frac{dx_1}{d\tau} = \frac{b_{\Delta}P_{\Delta}}{1 + b_{\Delta}P_{\Delta}} [k_1x_1 - x_3(k_{21}K_{23} + k_{31})] \quad (3)$$

where

$$k_1 = k_{12} + k_{13} \quad \text{and} \quad K_{23} = (x_2/x_3)_{eq}$$

Since

$$x_3 + x_2 = 1 - x_1 = x_3(1 + K_{23})$$

that is,

$$x_3 = (1 - x_1)/(1 + K_{23})$$

and since

$$K_{12} = k_{21}/k_{12}, \quad K_{13} = k_{31}/k_{13}, \quad K_{12}K_{23} = K_{13}$$

Eq. (3) becomes

$$-\frac{dx_1}{d\tau} = \frac{b_{\Delta}P_{\Delta}}{1 + b_{\Delta}P_{\Delta}} \times \left[ k_1x_1 - \frac{K_{13}}{1 + K_{23}} (1 - x_1)k_1 \right] \quad (4)$$

Equation (4) may be written in a synthetic form as

$$-dx_1/d\tau = M[x_1(1 + R) - R] \quad (5)$$

where

$$M = k_1b_{\Delta}P_{\Delta}/(1 + b_{\Delta}P_{\Delta}) \quad (6)$$

$$R = K_{13}/(1 + K_{23}) \quad (7)$$

For each set of runs performed at the same 1-butene partial pressure, the value of  $M$  is constant and Eq. (5) may be integrated to  $M\tau = -[1/(1 + R)] \ln[x_1(1 + R) - R]$  (8)

Linear plots of Eq. (8) for the runs performed at the same temperature and at various 1-butene pressures have been drawn and an example is reported in Fig. 2. From the slopes of such plots we obtained the values of  $M$  at various 1-butene partial pressures.

Rearranging Eq. (6) we have

$$1/P_{\Delta} = b_{\Delta}k_1(1/M) - b_{\Delta} \quad (9)$$

which is a linear relation between  $1/P_{\Delta}$  and  $1/M$ .

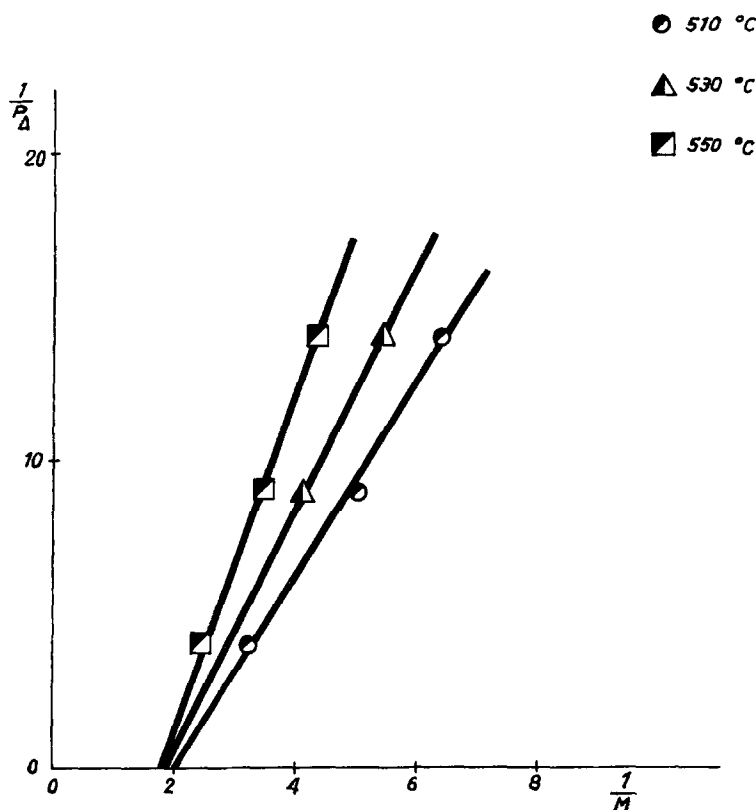


Fig. 3. Linear plots of Eq. (9).

The plots of this relation at the three temperatures are reported in Fig. 3. From the intercepts and from the slopes of the lines we obtained the values of  $b_{\Delta}$  and  $k_1$ , respectively, which are reported in Table 2.

TABLE 2  
VALUES OF  $k_1$  AND  $b_{\Delta}$  AT VARIOUS TEMPERATURES

$T$ (°C)	$k_1$ (moles/hr g cat.)	$b_{\Delta}$ (atm <sup>-1</sup> )
510°	0.500	6.34
530°	0.555	7.07
550°	0.606	8.75

Employing these values of  $k_1$  and  $b_{\Delta}$  we evaluated the plots of  $x_1$  vs.  $\tau$ , an example of which is shown in Fig. 4.

In Fig. 5 an example of plotting the change in composition of the system vs. contact time is given. The curves representing the *cis*- and *trans*-2-butenes have been calculated from the equilibrium relations.

As regards the runs performed in the

presence of ammonia, we assumed that this gas is adsorbed on the isomerization sites and it, therefore, competes with butenes in adsorption.

In such a case the general expression of a reaction rate is

$$r_{ij} = k_{ij} \frac{b_{\Delta} P_{\Delta} x_i}{1 + b_{\Delta} P_{\Delta} + b_A P_A} \quad (10)$$

where  $b_A$  is the adsorption equilibrium constant of ammonia (atm<sup>-1</sup>); and  $P_A$ , the ammonia partial pressure in the feed (atm).

The plot of Fig. 1 reveals that also for the runs performed in the presence of ammonia the *cis*- and *trans*-2-butenes are at equilibrium.

Since we have made our runs at constant ammonia partial pressure and at different contact times, the conversion of 1-butene may be expressed again by Eq. (6), provided that one redefines  $M$  as follows:

$$M = \frac{k_1 b_{\Delta} P_{\Delta}}{1 + b_{\Delta} P_{\Delta} + b_A P_A} \quad (11)$$

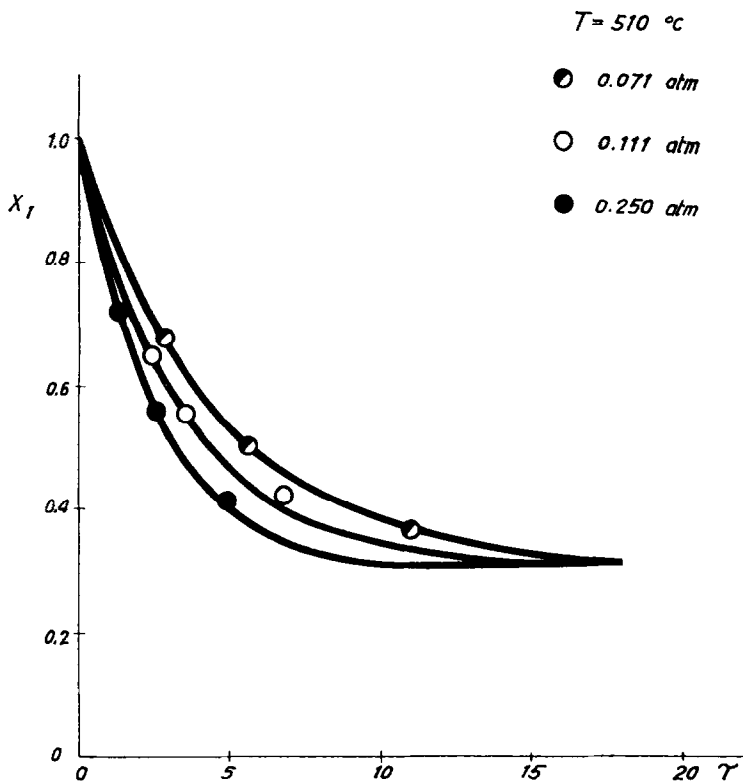


FIG. 4. 1-Butene disappearance vs. contact time at 510°C. Solid lines calculated from Eq. (8).

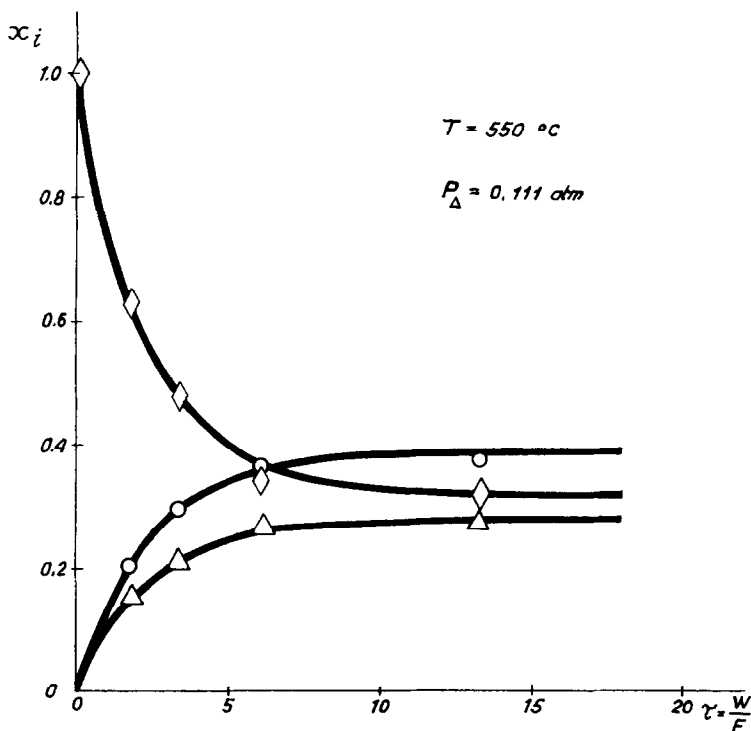


FIG. 5. Reaction of 1-butene at 550° and  $P_{\Delta} = 0.111\text{ atm}$ :  $\diamond$ , 1-butene;  $\circ$ , trans-2-butene;  $\Delta$ , cis-2-butene. Solid lines calculated from kinetic equations.

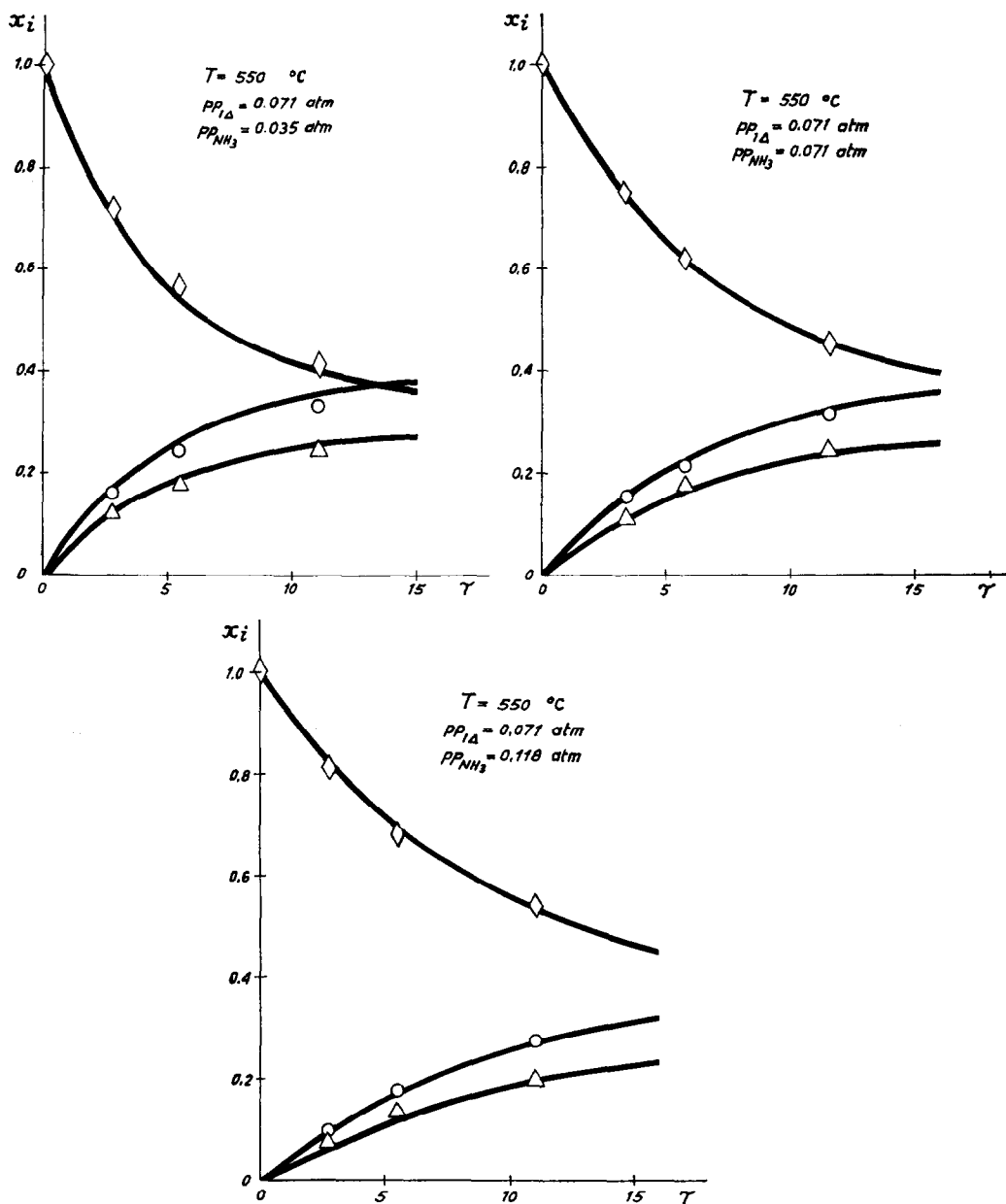


Fig. 6. Reaction of 1-butene at 550°C in the presence of ammonia:  $\diamond$ , 1-butene;  $\circ$ , *trans*-2-butene;  $\triangle$ , *cis*-2-butene.

The runs performed in the presence of ammonia have been interpreted assuming for  $b_A$  and  $k_1$  the values previously determined (Table 2). By means of calculations similar to the preceding ones we determined the value  $b_A = 30.5 \text{ atm}^{-1}$ . In Fig. 6 com-

plete conversion plots of the runs performed with ammonia are reported.

#### DISCUSSION

The ratio of *trans*-2-butene to *cis*-2-butene at the temperatures at which we operated

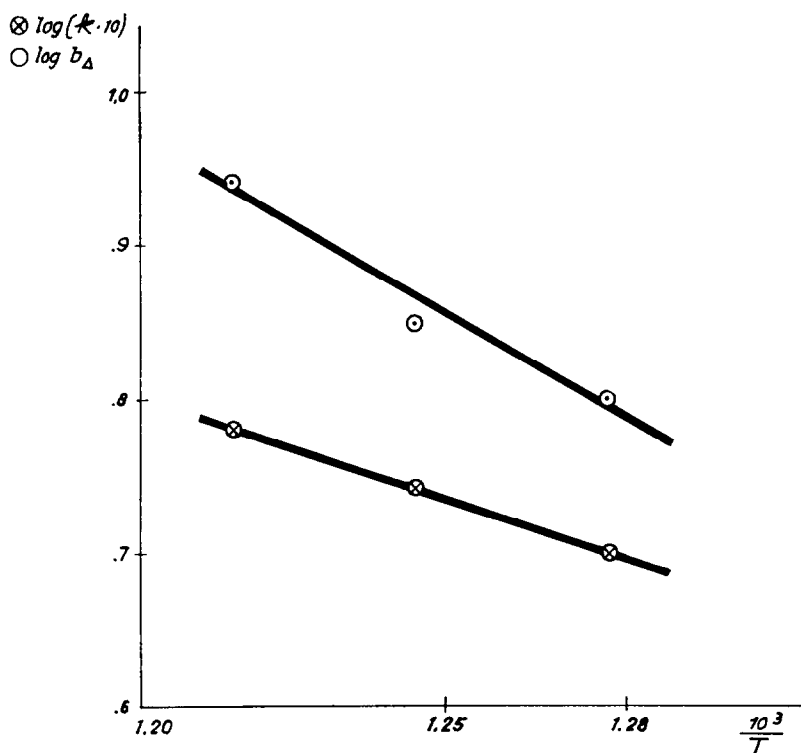


FIG. 7.  $\log b_A$  and  $\log k_1$  vs.  $1/T$ .

corresponds to that of thermodynamic equilibrium, even at the lowest contact times, and it is unaffected by the presence of a basic substance like ammonia in the reacting mixture. The presence of ammonia reduces the 1-butene to 2-butene isomerization reaction rate, according to a kinetic model in which ammonia competes with 1-butene in the adsorption on the active centers.

The 1-butene adsorption equilibrium constants increase with temperature. In Fig. 7 the plots of  $\log k_1$  and  $\log b_A$  vs.  $10^3/T$  are reported. In both cases the calculated values lie on a straight line; from the slopes of these lines the following values of activation energy of isomerization reaction and of adsorption enthalpy of 1-butene have been obtained:

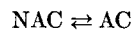
$$\Delta E^\ddagger = 6.87 \text{ kcal/mole}$$

$$Q = -\Delta H_a^\circ = -10.46 \text{ kcal/mole}$$

The negative value of adsorption enthalpy can be attributed to a thermal activation of the catalyst surface. Examples of such

activation have been previously found (6) and an extensive discussion of the dynamic behavior of the catalyst surfaces was given by Garcia de la Banda (7).

The reactant adsorption is connected with an endothermic activation equilibrium of active centers of the type



where NAC indicates a nonactivated center and AC an activated one. This fact may justify the apparent negative value of adsorption enthalpy.

Our findings reveal that the *cis-trans* isomerization reaction at temperatures above 500°C is very fast. Besides, the rate of this reaction is unaffected by the presence of ammonia, which otherwise is adsorbed on the same active centers that favor the isomerization reaction of 1-butene to 2-butene. The easy *cis-trans* 2-butene interconversion indicates that at high temperatures the thermal activation of such a reaction does not require any specific active center as in double-bond migration.



## ACKNOWLEDGMENTS

We are grateful to Dr. C. Cavenaghi for valuable help in experimental work. We are indebted to Italian Consiglio Nazionale delle Ricerche for financial aid.

## REFERENCES

1. HAAG, W. O., AND PINES, H., *J. Am. Chem. Soc.* **82**, 2488 (1960).
2. TUNG, S. E., AND MCININCH, E., *J. Catalysis* **3**, 229 (1964).
3. GERBERICH, H. R., AND KEITH HALL, W., *J. Catalysis* **5**, 99 (1966).
4. CARRÀ, S., FORNI, L., AND VINTANI, C., *J. Catalysis* **9**, 154 (1967).
5. VOGEL, H. H., AND MAY, N. C., *J. Am. Chem. Soc.* **68**, 550 (1946).
6. FORD, F. E., AND PERLMUTTER, D. D., *Chem. Eng. Sci.* **19**, 371 (1964).
7. GARCIA DE LA BANDA, J. F., Coloquio sobre Química Física de Procesos en Superficies Sólidas, Madrid, 1964.