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Received March 13, 1967

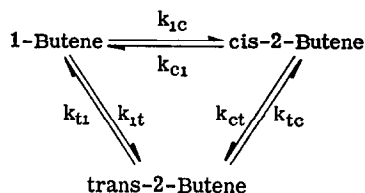
Selective Poisoning of Al_2O_3 Catalysts

In two recent Notes, Medema and Houtman (1, 2) reported evidence for two types of active centers for *n*-butene isomerization over gamma alumina. They based their claims on abrupt changes in certain product curves and on different cutoff points as reactions of each of the isomers were progressively poisoned with triethylamine in a microcatalytic reactor. It is the purpose of this communication to point out possible dangers in applying this technique and to offer an alternative explanation for their results.

Several investigators (3-9) have shown that *n*-butene isomerization reactions follow first order kinetics over acidic oxide catalysts. By making one of the reactants radioactive, it was possible for us (9) to follow to equilibrium simultaneously the conversion of *two* isomers over alumina in a static reactor, and these results could be quantitatively reproduced with a mathematical model based entirely on first order kinetics. All six relative rate constants, and also their temperature dependencies, were determined. Furthermore, neither poisoning nor selectivity changes with time, such as those reported by Medema and Houtman (1) in their Fig. 3, were observed with our alumina, which was prepared from the neutral hydrolysis of aluminum isopropoxide and was probably a mixture of eta and gamma alumina.

Although the two aluminas may be different, it is possible to use data from our catalyst to calculate reaction distribution patterns (Fig. 2) which have shapes very similar to those presented by these authors

(Fig. 1), *without assuming different numbers and/or types of active sites*. In our case the initial cis/trans ratio from 1-butene, i.e., the ratio of first order rate constants k_{1c}/k_{1t} in the reaction scheme



was 6.25 ± 0.2 at 23°C , and the difference in activation energy for the two paths was -1.8 ± 0.2 kcal/mole. (The "significant figures" given are those actually used in the calculations.) Correcting this value for the temperature difference would lead to a k_{1c}/k_{1t} ratio of 1.67 ± 0.4 at 250°C ; this value is almost within the limit of error in agreement with the low conversion cis/trans ratio (about 2.2) observed by Medema and Houtman (1) in their Fig. 1a. Considering the different sources of the two aluminas and the long temperature extrapolation for the cis/trans ratio, this is quite good agreement.

This value ($k_{1c}/k_{1t} = 1.67$), together with the cis/1-butene ratio from trans isomerization taken from Medema and Houtman's Fig. 1c ($k_{tc}/k_{t1} = 2.29$) and the three equilibrium constants of Benson *et al.* (10) at 250°C ($k_{c1}/k_{1c} = 0.55$, $k_{t1}/k_{1t} = 0.31$, and $k_{tc}/k_{ct} = 0.57$), provide five equations relating the six rate constants. Defining k_{1c} as 100 gives the sixth equation required to

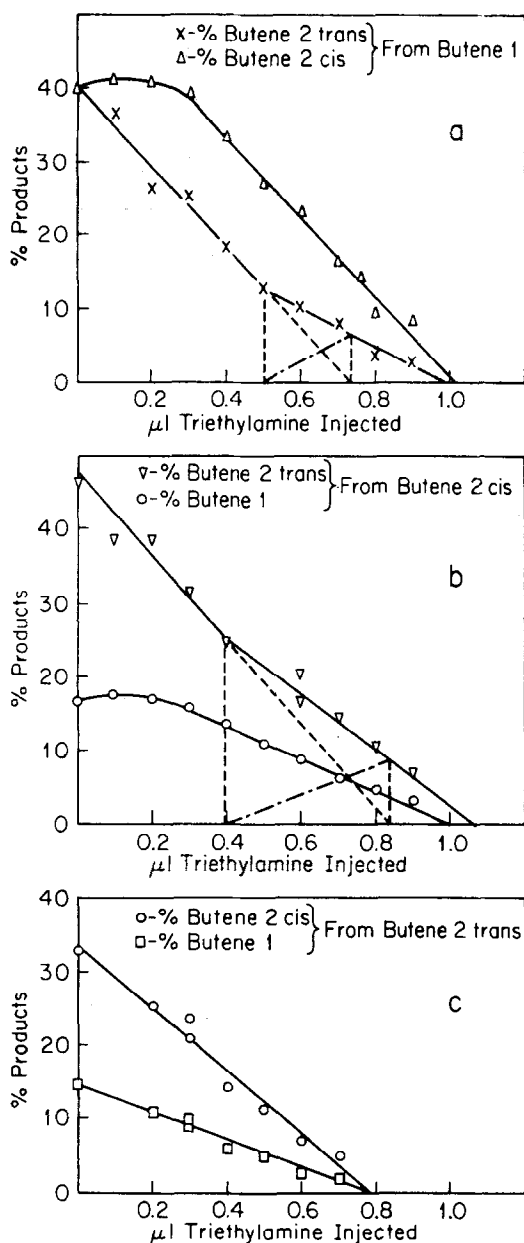


FIG. 1. Products formed on triethylamine-poisoned catalyst as a function of amounts of amine introduced. Preheated at 500°C; reaction temperature, 250°C; pulse experiment; contact time approx. 1 sec. (Copied from Fig. 1, ref. 1.)

calculate values for the relative rate constants under these conditions; they are

$$\begin{array}{ll}
 k_{1c} = 100.00 & k_{1t} = 60.00 \\
 k_{c1} = 54.61 & k_{ct} = 75.00 \\
 k_{t1} = 18.70 & k_{tc} = 43.02
 \end{array} \quad (2)$$

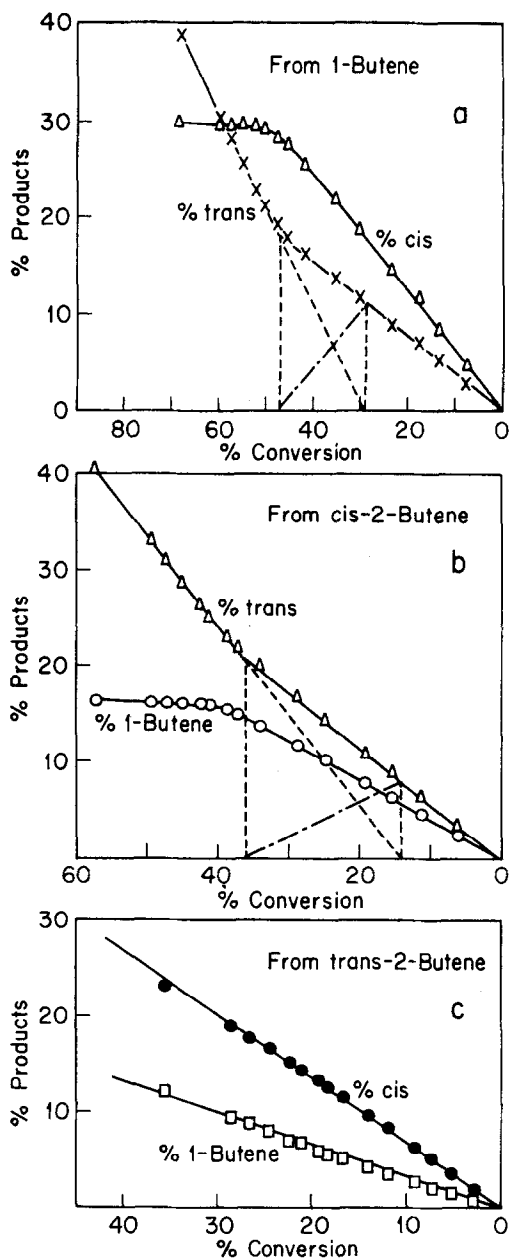


FIG. 2. Product distributions calculated on the basis of first order kinetics for the isomerization of three *n*-butenes at 250°C without assuming any selectivity changes during reaction. The relative rate constants are given in Table 1.

From these rate constants the calculated selectivity for cis conversion, k_{c1}/k_{ct} , of 0.73 is not far from the low conversion value of about 0.6 observed by Medema and Houtman (Fig. 1b).

TABLE 1
 PRODUCT DISTRIBUTIONS CALCULATED FROM ASSUMED FIRST ORDER
 RATE CONSTANTS FOR *n*-BUTENE ISOMERIZATION^a

Reaction time (arbitrary units)	% Reaction products								
	From 1-butene			From <i>cis</i> -2-butene			From <i>trans</i> -2-butene		
	cis	trans	Conv.	1-But	trans	Conv.	1-But	cis	Conv.
0.0005	4.6	2.8	7.4	2.5	3.5	6.0	0.8	2.0	2.8
0.0010	8.4	5.2	13.6	4.7	6.4	11.1	1.6	3.6	5.2
0.0015	11.7	7.1	17.8	6.4	8.9	15.3	2.2	5.1	7.3
0.0020	14.5	8.9	23.4	7.9	11.0	18.9	2.8	6.3	9.1
0.0030	18.8	11.6	30.4	10.3	14.4	24.7	3.6	8.3	11.9
0.0040	21.9	13.7	35.6	11.9	16.8	28.7	4.3	9.7	14.0
0.0060	25.5	16.4	41.9	13.9	20.1	34.0	5.1	11.5	16.6
0.0080	27.4	18.1	45.5	15.0	22.0	37.0	5.7	12.6	18.3
0.0100	28.3	19.3	47.6	15.5	23.2	38.7	6.0	13.3	19.3
0.0150	29.2	21.2	50.4	16.0	25.2	41.2	6.7	14.4	21.1
0.0200	29.4	22.8	52.2	16.1	26.5	42.6	7.1	15.2	22.3
0.0300	29.5	25.5	55.0	16.1	28.9	45.0	8.0	16.6	24.6
0.0400	29.6	28.0	57.6	16.2	31.1	47.3	8.8	17.8	26.6
0.0500	29.7	30.3	60.0	16.2	33.1	49.3	9.5	19.0	28.5
0.1000	29.9	38.8	68.7	16.4	40.6	57.0	12.2	23.3	35.5

^a Equations of Haag and Pines (5) for scheme of Eq. (1) were used with $k_{1c} = 100.00$, $k_{1t} = 60.00$, $k_{c1} = 54.61$, $k_{ct} = 75.00$, $k_{t1} = 18.79$, $k_{tc} = 43.02$. The equilibrium distribution at 250°C is 1-butene, 16.6%; *cis*-2-butene, 30.4%; *trans*-2-butene, 53.0%.

These rate constants may be used in the first order equations of Haag and Pines (4) to calculate product distributions as a function of time, and this has been done in Table 1. The percent of each product was then plotted against percent conversion (Σ % isomerized products) in Fig. 2 for each of the three isomers. The similarity in shape between these calculated curves and the experimental curves of Medema and Houtman (Fig. 1) is striking. Of course, the shapes of the curves will change if the rate constants are altered. The percent conversion scales (abscissas) in Fig. 2 are different for the various isomers because of the different equilibrium concentrations. However, the corresponding points on each of the curves represent the same reaction time (Table 1).

The only significant difference between the shapes of the experimental and calculated curves is the higher maximum for the *cis* isomer in Fig. 1a than in Fig. 2a. This difference resulted from the use of 1.67 for the selectivity ratio k_{1c}/k_{1t} in the calculations. Use of a somewhat higher value (e.g., 2.2) would have reduced the difference con-

siderably, but this value was chosen to demonstrate a reasonable correlation between their alumina and our GA-48. Of course, any alteration of this ratio would necessitate corresponding changes in the other selectivities to satisfy the thermodynamic condition

$$K = \frac{k_{1c}}{k_{c1}} \times \frac{k_{ct}}{k_{tc}} \times \frac{k_{t1}}{k_{1t}} = \frac{k_{1c}}{k_{1t}} \times \frac{k_{ct}}{k_{c1}} \times \frac{k_{t1}}{k_{tc}} = 1$$

Eq. Constant Selectivity (3)
 Product Product

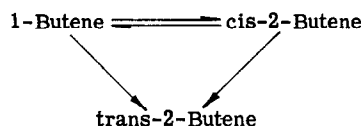
Equation (3) must hold near equilibrium, and we (9) have demonstrated that values of k_{ij} which fit this constraint reproduce the data over the entire range of *n*-butene reaction over a similar catalyst. The apparent low conversion selectivities of Medema and Houtman (*cis*/*trans* = 2.2, *trans*/1-butene = 1.7 and *cis*/1-butene = 2.3) give a value of about 1.6 for K . However, the true selectivity ratio could be considerably different from the apparent *cis*/1-butene ratio calculated from Fig. 1c. This method of determining k_{tc}/k_{t1} is not a sensitive one (8) (the lowest conversion point corresponded to about 8%) and could quite easily ac-

count for the authors' K value being different from unity.

The calculated curves of Fig. 2 were based solely on first order kinetics and did not involve changes in selectivity with time. It is possible that the poisoning with triethylamine depicted in Fig. 1 also affected only the percent conversion and did not alter the selectivity or relative numbers of active sites on which the different reactions occurred. In other words, the two straight line segments for formation of the *trans* isomer in both Figs. 1a and 1b can be explained exclusively on the basis of first order kinetics. It is therefore hazardous to use such a technique to prove the existence of more than one type of active site. It is still possible that each of the three *n*-butene reaction paths may take place on a different type of site, but experiments such as these probably do not demonstrate the phenomenon.

The different "cutoff" points on the triethylamine poisoning curves for the various isomers are interesting, but again the scatter in the data makes definite calculations of the numbers of "A- and B-type" sites rather tenuous. Since different catalyst samples were used in obtaining each of the curves in Fig. 1, a poison (e.g., butadiene) present only in the *trans*-2-butene could have been responsible for the early termination of the activity in Fig. 1c. The authors contend (1) that "sites which are poisoned in the second instance have no activity for *trans*-2-butene conversion and only limited activity for *trans*-2-butene formation." It is difficult to rationalize this statement in view of the law of microscopic reversibility since the reactions are all first order and rever-

sible. If the statement were true, one would expect only *trans*-2-butene at equilibrium after the most readily poisoned sites had been eliminated, i.e., the reactions would follow the scheme



rather than the scheme in Eq. (1).

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum.

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Received May 26, 1967

Selective Poisoning of Al_2O_3 Catalysts—A Reply

The effort of Hightower (1, preceding paper) to explain our previously published results (2) of poisoning experiments on a simple kinetics basis is very interesting.

However, his results, though seemingly in agreement with ours, are in fact on a number of important points strikingly different.

(1) The abscissas of our graphs and the