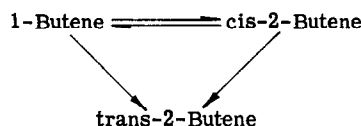


count for the authors' K value being different from unity.

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).

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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

graphs of Hightower are not equal, which makes comparison difficult. When our data are plotted as a function of total conversion all curves will, of course, start at the same point of the horizontal axis (zero conversion). However, in the graphs presented in our article the product formation has in fact been related to a catalyst surface property and it was found that the isomerization of *trans*-2-butene was completely poisoned with less amine than the isomerization of the other butenes. This was the main argument for accepting two types of active centers. The scatter in our data is rather small and insufficient to serve as an explanation for this effect, as was suggested by Hightower. Though the measurements with the various olefins were carried out using different samples of the same catalyst batch, the phenomena were found to be reproducible. They were also observed with aluminas of different origin. Moreover, the constant activity found for each catalyst sample in about six injections of olefin before adding amine indicate that none of the olefins contained any poison themselves.

(2) The kinetic analysis made by Hightower was done for a combination of k_{ij} values which were not in agreement with those found by us. A quantitative analysis even shows that it is impossible to select values for k_{ij} which provide a good fit for all conversion data found by us. The deviations observed are of a systematic nature due to the good reproducibility of our measurements. These deviations can be explained by one or both of the following facts: (a) the reactions are not first order over the full conversion range; (b) the reaction paths for the interconversion of the olefins are not equivalent. As the first order kinetics has been well proven, the

second explanation seems to be valid. This is confirmed by the fact that the ratio

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

was found to be unequal to 1. Of course, there is some uncertainty in the values for $k_{1c}/k_{1t} = 2.2$; $k_{ct}/k_{c1} = 2.0$; $k_{tc}/k_{t1} = 2.2$ deduced from the initial conversion rates in our experiments. However, the value for $K = 2.0$ deduced from them is very different from the theoretical value. Moreover such strong deviations have also been observed by others at small conversions (3).

(3) Our remark that certain sites have no activity for *trans*-2-butene conversion and only a limited activity for *trans*-2-butene formation was only used as a preliminary conclusion from the experimental data. It is clear that such a conclusion has only limited validity because a very small reaction rate could easily be overlooked under the circumstances of these experiments. At the end of our article it was clearly shown by us that we did not accept such sites to be completely inactive. This activity will be sufficient to guarantee the attainment of chemical equilibrium.

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