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Study on the Pulse Reaction Technique

II. Dealkylation and Disproportionation of Cumene

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The catalytic cracking of cumene on a silica-alumina catalyst was studied by the pulse technique with a rectangular pulse. The effect of pulse width on the conversion predicted in the previous paper was verified experimentally: The conversion increases with decreasing pulse width, and the reverse reaction can be neglected when pulse width is zero, where the relation between the conversion and the contact time is the same as that usually observed in the first order irreversible reaction. The activation energy of the forward reaction was found to be 24.4 kcal/mole from the conversion at zero pulse width. The effect of pulse width on the yield of diisopropylbenzene was also studied. The yield of diisopropylbenzene was independent of pulse width, from which it was concluded that diisopropylbenzene was formed in the disproportionation of cumene.

It is well known that some results obtained by the pulse technique differ from those by the flow technique. In the preceding paper (*1*) the authors made a theoretical analysis of the pulse technique on several typical reactions for the purpose of exposing the characteristics of the pulse technique and obtained the following results. For linear reactions there is no difference between the techniques, while with nonlinear reactions, sometimes, the differences are quite remarkable. They are caused mainly by the difference in the initial concentration, the lowering of product concentration owing to the different moving velocity from the reactant, and the separation among the components due to the different strength of adsorption. In the reaction of the sort $A \rightleftharpoons R + S$, the last factor results in larger conversion than that in the flow technique. The rate of the reverse reaction, $R + S \rightarrow A$, falls because R, once separated from S, can not react any more. The difference in conversion from the flow technique rises with decreasing pulse width, t_0. When t_0 is larger the separation is so incomplete that the conversion is close to that in the flow technique, but when t_0 is sufficiently small most of R is separated from S and the conversion is approximately equivalent to that without the reverse reaction. Plotting the conversion against pulse width and extrapolating it to zero, one can obtain the conversion without the reverse reaction, from which kinetic constants of the forward reaction can be determined.

In the present paper an experimental verification of such an effect of pulse width was made from the catalytic cracking of cumene. Echigoya *et al.* (*2*) studied this reaction and showed that not only propylene but also benzene were separated from cumene in a column packed with a silica-alumina catalyst. In the previous paper analysis was made on the case of $u_A = u_S$ and $u_R \neq u_S$, but when $u_A \neq u_S$ the similar dependency of the conversion on the pulse width may be obtained, as is easily expected from the similarity of the results between $A \rightleftharpoons R + S$ and $A \rightleftharpoons 2R$.

In the catalytic cracking of cumene a

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small amount of diisopropylbenzene was formed. The effects of the pulse width and of the cumene partial pressure on the yield of diisopropylbenzene have also been studied, and the mechanism of diisopropylbenzene formation is discussed.

EXPERIMENTAL

The catalyst was a commercial silica-alumina cracking catalyst with a particle size of ~100–150 mesh and containing 13.4% Al_2O_3. Extra pure grade cumene was used with further purification by percolation through a column packed with silica gel. It was reported that essentially all of the impurities of a polar type could be removed from cumene by this treatment (*3*). The apparatus used in this study was a conventional pulse reactor, which consisted of a gas chromatograph modified by the introduction of a small reactor between the sample inlet and the analytical column. The catalyst was held by small plugs of Pyrex glass wool in the Pyrex glass reactor with an inside diameter of 5 mm. It was activated by heating in air at 450°C for 3 hr and then its catalytic activity was stabilized by continuous reaction for 100 min per gram of catalyst to avoid initial activity decline. The temperature was measured with a thermocouple adjacent to the packed section of the reactor. The analysis of cumene and products was carried out with a 3 m by 4 mm column packed with Silicone Oil D.C. 550 on Celite 545 at 102°C. Hydrogen was used as a carrier gas, it was passed through a molecular sieve column installed before the sample inlet to remove humidity. Cumene was fed as a rectangular pulse by the aid of a microfeeder. It was constructed using a synchronous 2-rpm motor to spin a linear screw, which drives a plunger of a tuberculin-type syringe at a constant velocity, as shown in Fig. 1. By this feeder cumene could be sent in at a constant partial pressure during the time corresponding to the pulse width. The pulse width was altered in no particular order to avoid the effect of activity decline due to "coke" or polymer lay-down on the surface.

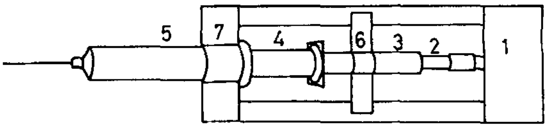

FIG. 1. Microfeeder; 1, synchronous motor; 2, male screw; 3, female screw; 4, plunger of syringe; 5, syringe; 6, screw holder; 7, syringe holder.

RESULTS AND DISCUSSION

The shape of the inlet pulse was determined by injecting cumene just before the detector. The chromatogram obtained in such a way showed that the inlet pulse could be regarded as a rectangular pulse. The standard reaction conditions were as follows: reaction temperature, 300°C; the weight of catalyst used, 0.4 g; hydrogen carrier gas flow rate, 40 ml/min; total pressure, 1.4 atm; and the partial pressure of inlet cumene, 0.206 atm. In any case five peaks appeared on each chromatogram: propylene, benzene, cumene, and two small peaks. They were identified as the isomers of diisopropylbenzene, which is formed by the disproportionation of cumene. Detailed discussion concerning the matter will be made later. The conversion by dealkylation of cumene, X, and the yield of diisopropylbenzene, Y_D, were calculated from the benzene ring balance of the effluents, by the following equations:

$$X = \frac{\text{benzene} - \text{diisopropylbenzene (moles)}}{\text{cumene} + \text{benzene} + \text{diisopropylbenzene (moles)}}$$

$$Y_D = \frac{\text{diisopropylbenzene (moles)}}{\text{cumene} + \text{benzene} + \text{diisopropylbenzene (moles)}}$$

The dependency of the conversion on the pulse width, t_0, obtained experimentally in the present study agrees well with that predicted theoretically [Fig. 13 in the preceding paper (*1*)]; the conversion decreases with increasing pulse width, as shown in

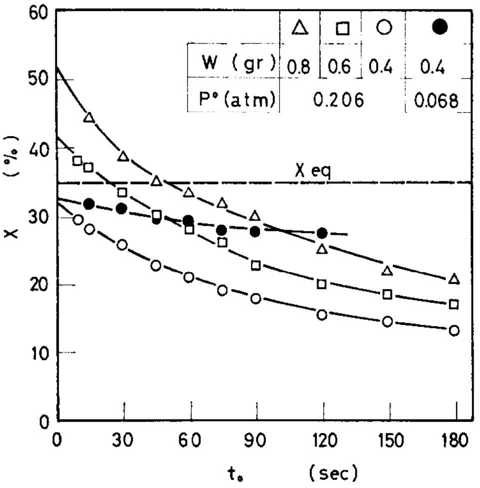

Fig. 2. Dependency of conversion on pulse width at 300°C.

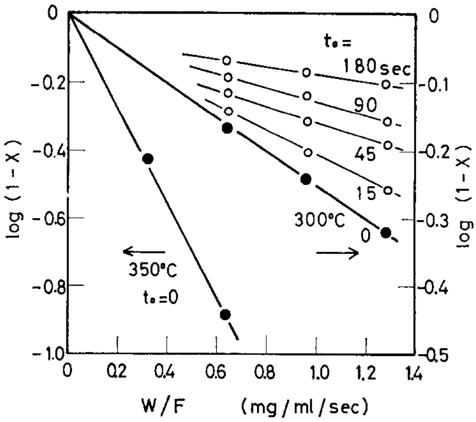

Fig. 3. Rate plot for first order irreversible reaction at different pulse widths.

Figs. 2 and 4. Such dependency could be due to catalyst poisoning due to "coke" or polymer lay-down on the surface, if the pulse width had been steadily increased from one pulse to the following one. In the present study, however, the catalytic activity was stabilized by the continuous reaction to avoid initial activity decline, and the pulse width was altered in no particular order, that is, using small–longer–smaller pulse widths. Therefore such dependency should be due to the characteristics of the pulse technique. As mentioned in the previous paper, it arises from the separation between the products. If $t_0 = 0$, the products are separated from each other so completely that the reverse reaction can not proceed and the conversion is equivalent to that in the irreversible reaction, which is confirmed by the proportionality between $\log(1-X)$ and W/F at $t_0 = 0$, shown by the darkened points in Fig. 3. With increasing pulse width the effect of the separation decreases and the role of the reverse reaction becomes important, which results in the lowering of conversion. This explanation is supported by the small dependency of X on t_0 at low partial pressure of cumene, given by the darkened points in Fig. 2. With decreasing cumene partial pressure, the equilibrium conversion increases, that is, the role of reverse reaction becomes less important. It follows that even if the separation is incomplete the conversion does not decrease so much, and the effect of the pulse width is smaller than that in the high partial pressure of cumene. The conversion at $t_0 = 0$, X_0, at low partial pressure agrees with that at high partial pressure, which indicates the order of the forward reaction is unity.

The relation between $\log(1-X)$ and W/F is shown in Fig. 3. It is verified by the proportionality between $\log(1-X_0)$

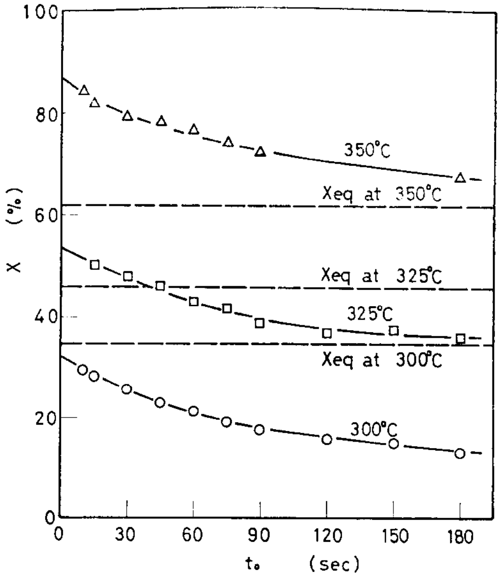

Fig. 4. Dependency of conversion on pulse width at different reaction temperatures.

and W/F given by the darkened points that the reverse reaction can be neglected when $t_0 = 0$, and that the forward reaction is the one with the first order kinetics. The deviation from proportionality increases with increasing pulse width, which suggests that the role of the reverse reaction becomes important.

The effect of pulse width on the conversion was studied also at 325° and 350°C. The reaction rate constants of the forward reaction were determined from the slope of the straight line plot of $\log(1 - X_0)$ versus W/F at each temperature, and from those the activation energy was found to be 24.4 kcal/mole, which agrees with that obtained by Pansing *et al.* (*4*).

It has already been verified from the dehydrogenation of cyclohexane on Pt-Al_2O_3 catalyst (*5*) that the reaction can proceed over the equilibrium conversion in the pulse technique. It is worth noting that the larger conversion than that in the equilibrium state was obtained in spite of a small quantity of catalyst. At 300°C extremely small pulse width is required to get larger conversion than the equilibrium value, as shown in Fig. 2. At 350°C, however, even when $t_0 = 180$ sec, the conversion is larger than that in the equilibrium, as shown in Fig. 4.

The yield of diisopropylbenzene is independent of pulse width, but depends on the initial partial pressure of cumene, as shown in Fig. 5. It follows that diisopropylbenzene is considered to be formed in the disproportionation of cumene and the order of diisopropylbenzene formation is larger than unity. If it is formed in the alkylation of cumene with propylene ($C + P \rightleftharpoons D$), Y_D will decrease with decreasing pulse width because of the separation between cumene and propylene. When the pulse width is sufficiently small, most of the propylene is separated from cumene, and the alkylation does not proceed because propylene once separated from cumene can not react any more. However such dependency of Y_D on t_0 was not observed experimentally: As mentioned above, Y_D is independent of t_0, and furthermore even when t_0 is about a few seconds (such small pulse width can be obtained by injecting cumene with a microsyringe), a considerable amount of diisopropylbenzene is obtained. For that reason it was concluded that diisopropylbenzene is not a product of the alkylation of cumene with propylene.

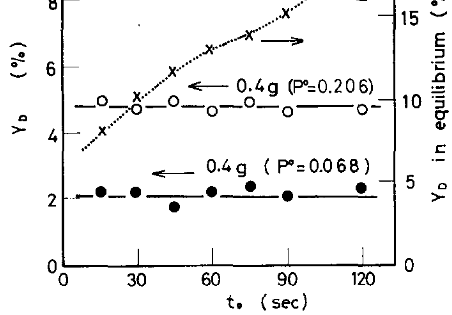

FIG. 5. Dependency of yield of diisopropylbenzene on pulse width at 300°C.

On the other hand, if diisopropylbenzene is formed by the disproportionation of cumene ($2C \rightleftharpoons D + B$), it is not necessary to consider the separation between the reactants. However the separation between the products must be taken into consideration, because the reverse reaction can not be neglected. The equilibrium constants were estimated to be 0.091, 0.215, and 0.121 respectively for *o*-, *m*-, and *p*-diisopropylbenzene at 300°C by the group contribution method of Anderson, Beyer, and Watson (*6*). As easily expected, diisopropylbenzene may be separated from benzene. If the dealkylation of cumene were absent, Y_D should increase with decreasing pulse width because of the separation between the products, similarly to the case of dealkylation. However in the actual case, the cumene partial pressure decreases with decreasing pulse width, because the conversion of dealkylation increases, as shown in Figs. 2 and 4. Therefore the rate of disproportionation significantly decreases with decreasing pulse width because the order of the reaction is larger than unity. Further, the equilibrium yield of diisopropylbenzene decreases with decreasing cumene partial pressure or increasing conversion of dealkylation: Y_D in the equilibrium is equivalent to 0.254, 0.186, 0.132, and 0.089, respectively, at $X = 0.2$, 0.3, 0.4, and 0.5. Thus Y_D in the equilibrium decreases with decreasing pulse width, as shown by the dotted line in Fig. 5 which corresponds to the case of $W = 0.8$ g. Such an effect of lowering cumene partial pressure may counterbalance the effect of the separation between the products, which may result in the absence of the dependency of the yield of diisopropylbenzene on the pulse width shown in Fig. 5.

REFERENCES

1. HATTORI, T., AND MURAKAMI, Y., *J. Catalysis* **10,** 114 (1968).
2. ECHIGOYA, E., AND OCHIAI, Y., *Kogyo Kagaku Zasshi* **69,** 1858 (1966).
3. PLANK, C. J., AND NACE, D. M., *Ind. Eng. Chem.* **47,** 2374 (1955).
4. PANSING, W. F., AND MALLOY, J. B., *Ind. Eng. Chem., Process Design & Develop.* **4,** 181 (1965).
5. MATSEN, J. M., HARDING, J. W., AND MAGEE, E. M., *J. Phys. Chem.* **30,** 522 (1965).
6. ANDERSON, J. W., BEYER, G. H., AND WATSON, K. M., *Natl. Petrol. News, Tech. Sec.* **36,** R376 (July 5, 1944).