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The Catalytic Dehydrogenation of Ethylbenzene and Cumene Over Catalysts Containing Uranium Oxide

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The dehydrogenation of ethylbenzene to styrene and of cumene to α-methylstyrene has been investigated in a fixed bed reactor over bismuth uranate Bi_2UO_6 and uranium oxide as catalysts, at temperatures from 420 to 520°C. Selectivities of 97% at a conversion of 38% for styrene and of 96% at a conversion of 66% for α-methylstyrene have been obtained in this study. Under reaction conditions Bi_2UO_6 loses 67 wt% of its oxygen and metallic bismuth is formed. Uranium oxide is reduced to UO_2. The reaction pattern on both catalysts changes during the reduction. This investigation is mainly concerned with the performance of the reduced catalysts. A kinetic model, which takes into account the chemisorption of the saturated reactants and of the unsaturated reaction products, has been used to interpret the experimental data. Energies of activation are 34 kcal mol^{-1} for the ethylbenzene dehydrogenation and 27 kcal mol^{-1} for the cumene dehydrogenation. By-products formed from ethylbenzene are benzene and toluene, while cumene produces benzene, toluene, ethylbenzene and styrene.

NOMENCLATURE

C	Concentration of ethylbenzene or cumene under reaction conditions, mmol $liter^{-1}$.
C_S	Concentration of hydrocarbon with saturated side chain, mmol $liter^{-1}$.
C_U	Concentration of hydrocarbon with unsaturated side chain, mmol $liter^{-1}$.
C_H	Concentration of hydrogen, mmol $liter^{-1}$.
C_0	Concentration of ethylbenzene or cumene under reaction conditions before entering the catalyst bed, mmol $liter^{-1}$.
C_i	Concentration of component i in the reaction gas, mmol $liter^{-1}$.
k_1	Surface reaction rate constant, mmol $(g\ cat.\ sec)^{-1}$.
K_{eq}	Equilibrium constant of the dehydrogenation reaction, mmol $liter^{-1}$.
K_i	Adsorption constant of component i, liters $mmol^{-1}$.
j	Index number of experimental data at one reaction temperature.
r	Reaction rate, mmol $(g\ cat.\ sec)^{-1}$.
T	Reaction temperature, °C.
τ	Contact time $= \epsilon W/[F\rho(1-\epsilon)]$, sec, since $\epsilon = \pm 0.5 \rightarrow \tau = W/F\rho$.
ϵ	Porosity of catalyst.
W	Catalyst weight, g.
F	Feed rate ethylbenzene or cumene + nitrogen, liters sec^{-1}.
ρ	Density of catalyst, g $liter^{-1}$.

INTRODUCTION

The most important process for styrene manufacture is the dehydrogenation of ethylbenzene, usually carried out at temperatures of about 600°C over metal oxide catalysts in a steam atmosphere. In this process selectivities of about 92% are reached at a maximum conversion level of about 40%. In spite of the importance of the process and the considerable number of publications on the technical performance of the catalytic dehydrogenation and on the dehydrogenation catalysts, few kinetic data have been published so far (*1–3*). The dehydrogenation of cumene to α-methylstyrene is also of importance and here kinetic data are even more scarce (*4, 5*). The oxidative dealkylation of toluene over bismuth uranate has been studied by De Jong (*6–8*), who also attempted to dealkylate ethylbenzene. Considerable amounts of styrene were produced with high selectivity. Our investigations showed that uranium dioxide is also an active but more stable dehydrogenation catalyst. Only in the older literature uranium trioxide is mentioned as a component of dehydrogenation catalysts (*9, 10*).

In this paper we describe the behavior of bismuth uranate and uranium oxide as dehydrogenation catalysts and give a kinetic model for the reaction on uranium oxide.

METHODS

Preparation of bismuth uranate and uranium oxide. Bismuth uranate was prepared as described by De Jong (*6, 8*) who has also surveyed the properties of various mixed oxides of bismuth and uranium. Dried bismuth uranate Bi_2UO_6 was calcined at 600°C for 24 hr. The orange-brown product was broken and the sieve fraction 0.15–0.30 mm used as catalyst.

The oxides of uranium form a very complex system, often showing large deviations from stoichiometry. The stoichiometric oxides include UO_2 (brown), U_3O_8 (dark green), and UO_3 (orange-yellow). According to Gmelin (*11*), $UO_{2.8}$ (brown-green) to $UO_{2.9}$ (light-grey-brown) are known, both being oxygen-excess U_3O_8. Oxides with stoichiometry $UO_{2.2}$ to $UO_{2.6}$ are black. At least six polymorphs of UO_3 and also an amorphous phase from this oxide are known. Calcination of ammoniun uranates or uranyl nitrate at about 450°C gives an oxide UO_3, which can be reduced at 650 to 800°C to UO_2. This oxide cannot be reduced further, not even by hydrogen at high temperatures and pressures.

Uranium oxide was prepared by dissolving uranyl acetate [$(CH_3COO)_2UO_2 \cdot 2H_2O$ Merck p.a.] in warm water. An excess of a concentrated ammonia solution was added. The yellow precipitate $UO_3 \cdot xNH_3 \cdot yH_2O$ was filtered off and washed with water. The precipitate was dried at 135°C during 24 hr and the product was finally calcined at 600°C for 24 hr. The resulting dark green grains were broken and the sieve fraction 0.15–0.30 mm was used as catalyst. When we assume that heating in air at 850°C leads to U_3O_8 (*12*), the measured weight loss implied a stoichiometry of $UO_{2.73}$ for our catalyst. Reduction of the catalyst in a thermobalance at 530°C with hydrogen to UO_2 gave loss in weight that indicates the formula $UO_{2.71}$. The dark green color of the catalyst closely resembled the color of U_3O_8. The specific surface area of the uranium oxide catalyst determined according to the BET method using nitrogen as adsorbate, was 6.3 $m^2\ g^{-1}$.

Apparatus and Analysis

Figure 1 shows a flow sheet of the apparatus. A constant flow of nitrogen was passed through a thermostated vaporizer, filled with ethylbenzene (or cumene). The nitrogen was freed of oxygen by passing it over a reduced BTS catalyst. The nitrogen–

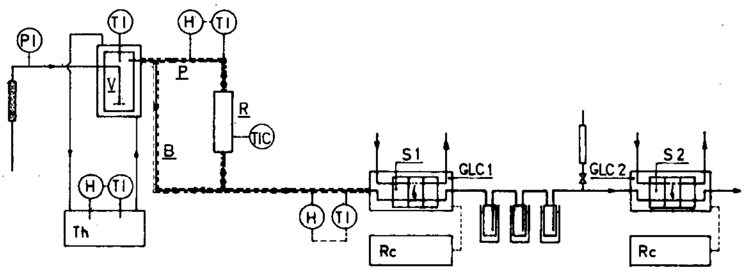

FIG. 1. Apparatus for the dehydrogenation of ethylbenzene: (V) vaporizer; (P) preheater; (B) bypass; (R) reactor; (Th) thermostated bath; (S_1, S_2) sample valves; (GLC_1, GLC_2) gas chromatographs; (Rc) recorder.

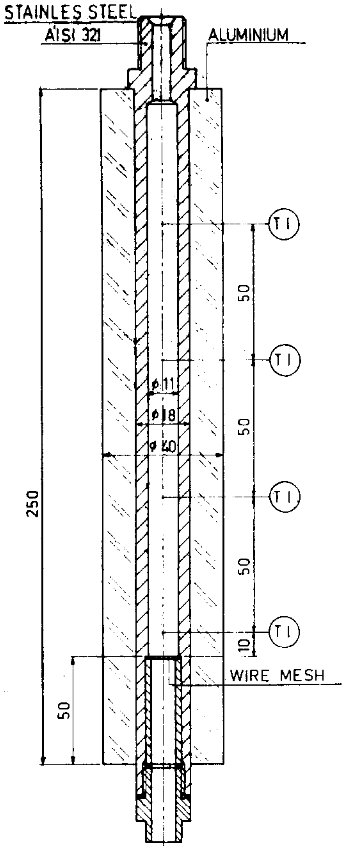

FIG. 2. Reactor.

hydrocarbon mixture passed either via preheater P through reactor R or flowed directly via bypass B to the sample valve S_1 (*13*).

The stainless steel fixed bed reactor, shown in Fig. 2, was electrically heated. The temperature was measured by a thermocouple in the middle of the fixed bed and controlled to ±1°C with a Eurotherm Thyristor controller. The catalyst was supported by a fine wire mesh.

The reactor feed or the reaction products were introduced into an analysis system consisting of two gas chromatographs, separated by a series of cold traps (temperature −20°C). The first gas-chromatograph GLC_1, equipped with a flame ionization detector, enabled benzene, toluene, ethylbenzene, cumene, styrene and α-methylstyrene to be determined, while on GLC_2 (katharometer detector), the uncondensed gases, mainly hydrogen (and carbon dioxide formed during reduction of the catalyst) were determined. Other details of the GLC analysis are given in Table 1.

TABLE 1

GAS CHROMATOGRAPHIC CONDITIONS[a]

Component	Relative retention times of the products
Benzene	0.22
Toluene	0.44
Ethylbenzene	0.75
Cumene	1.00
Styrene	1.46
α-Methylstyrene	2.56
β-Methylstyrene	3.91
Indene	5.87

[a] Hydrocarbon analysis: Column length, 1 m; internal diameter, 2 mm; filled with 20% polyethylene glycol adipate ester on Gaschrom Q; temp, 130°C; carrier gas, nitrogen, 20 ml min^{-1}; detector, flame ionization detector. Hydrogen and carbon dioxide analysis: Column length, 20 cm; diameter, 0.25 in., filled with active charcoal; temp, 60°C; carrier gas, nitrogen, 50 ml min^{-1}; detector, hot wire detector.

Dehydrogenation Experiments

The reactor was filled with a mixture of catalyst and silicon carbide (both sieve fraction 0.15–0.30 mm) in the ratio of 1:7.5 by weight, thereby improving isothermal conditions and preventing channel formation because of catalyst shrinkage in the bed during the reduction. Before the start of the experiments the system was purged with nitrogen and thereafter the vaporizer, which had been set to the desired temperature, was switched into the system. The product stream was sampled and analyzed at 4-min intervals. The reactor feed was analyzed before and after each experiment.

Experiments with Bismuth Uranate

Ethylbenzene, at a partial pressure of 5.35 mm Hg, was led over 0.87 g bismuth uranate at 490–570°C and nitrogen flows of 2.5 and 5 liters hr^{-1}. Conversions of ethylbenzene, production of styrene, benzene and toluene, and formation of H_2 and CO_2 were evaluated. From the oxygen balance also the degree of catalyst reduction was calculated.

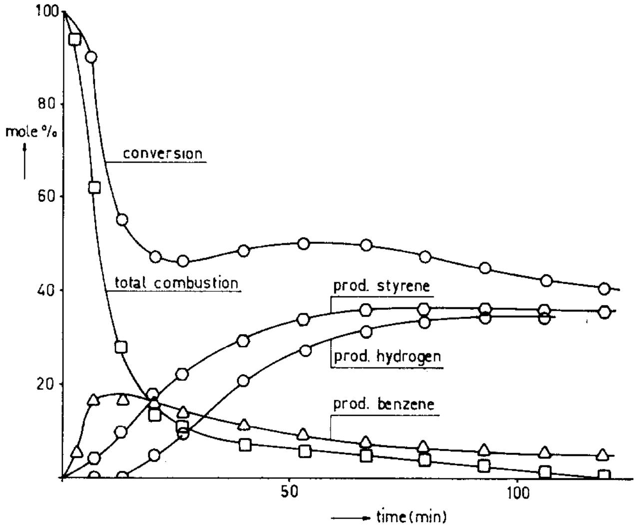

FIG. 3. Reduction of Bi_2UO_6 to Bi_2UO_2 with ethylbenzene: Reaction temp, 490°C; Bi_2UO_6, 0.87 g; feed, 2.5 liters hr^{-1} N_2 and 0.69 mmol hr^{-1} ethylbenzene.

The course of the product composition during a typical experiment is shown in Fig. 3. The reaction starts with complete combustion of ethylbenzene to CO_2 and water. Very soon the formation of benzene by oxidative dealkylation is observed while the styrene formation starts somewhat later. Initially the hydrogen formed together with styrene is completely oxidized to H_2O but after 10 min hydrogen starts to appear among the reaction products. During an experiment the bismuth uranate lost 67 wt% of its oxygen, resulting in metallic bismuth and UO_2. A closely analogous result has been obtained by Batist *et al.* (*20*) during the reduction of bismuth molybdate. On completely reduced bismuth uranate the amounts of styrene and hydrogen in the reactor effluent gas are equal.

After reoxidation of the catalyst a similar overall behavior was maintained but the actual conversion as a function of the degree of reduction of the bismuth uranate varied in an erratic way. The X-ray diagrams of fresh and reoxidized catalyst differed markedly, as shown in Table 2. These data indicate that reoxidation does not completely restore the original structure. A few weak lines, probably from metallic bismuth are to be seen in the X-ray diagram of the used catalyst. Careful reoxidation with 0.5 ml pulses of air below 100°C of a sample that had been reduced with hydrogen at 480°C gave a product that showed strong metallic bismuth lines.

We also reduced fresh bismuth uranate

TABLE 2

X-RAY DATA FOR FRESH AND OF USED REOXIDIZED BISMUTH URANATE, AND BISMUTH METAL

d values (Å)		
Fresh Bi_2UO_6	Used Bi_2UO_6	Bismuth metal
3.25	3.16	3.28
2.81	2.73	
	2.48	
	2.32	2.27
1.99	1.92	
1.69	1.67	
	1.63	1.64
1.61	1.57	
	1.51	
1.47		
1.39	1.31	
1.29	1.26	1.26
1.26	1.25	1.25
	1.22	
1.15	1.12	1.12
1.08	1.05	
1.01		

in a Mettler thermobalance at 500°C in a hydrogen stream. After the experiment, a metallic grey mirror had appeared in the colder part of the balance. The mirror dissolved easily in dilute nitric acid, and the presence of bismuth was proved by the cinchonine spot test (*14*). We concluded, therefore, that under reducing conditions bismuth uranate is unsuitable as a dehydrogenation catalyst. Because reduced bismuth uranate gave good (though irreproducible) styrene yields and conversions, we investigated the two components bismuth oxide and uranium oxide separately and found that UO_2 is probably the active component for the dehydrogenation.

Experiments with Uranium Oxide

The catalyst was reduced to UO_2 at 500°C with 2.5 liters hr^{-1} of a nitrogen-ethylbenzene mixture as shown in Fig. 4. The reaction product composition changes in the same way as during the reduction of bismuth uranate, but the reduction and thus the total combustion rates are higher. No decline in the dehydrogenation activity of UO_2 was noted during a run for 72 hr at 500°C and an ethylbenzene vapor pressure of 5.35 mm Hg.

Results of the experiments with the reduced catalyst at a temperature of 520°C are summarized in Table 3. Similar sets of experiments have been carried out at 460, 480, and 500°C. Some of the results are plotted in Fig. 5. In these figures only the ethylbenzene conversions are plotted, because in all these experiments the selectivities for styrene were on the average 95% and never below 90%, while the remaining products, benzene and toluene, were formed in almost equal amounts. The highest space velocity used in these experiments was 0.6 g ethylbenzene/g catalyst hr.

In the same way as described above, dehydrogenation experiments were carried out with cumene, but in these experiments 480°C was chosen as a maximum reaction temperature, because at 500°C the activity of the catalyst decreased slowly, probably because of the deposition of carbon on the catalyst. The results of these experiments at 480°C are summarized in Table 4. Corresponding results have been obtained at 435, 450 and 465°C and some of the results are plotted in Fig. 6. Here again only the cumene conversions are plotted, because the selectivities for α-methylstyrene were about 95%. Other products formed in these experiments were benzene, toluene, ethylbenzene and styrene, but no β-methylstyrene could be detected in the reaction product.

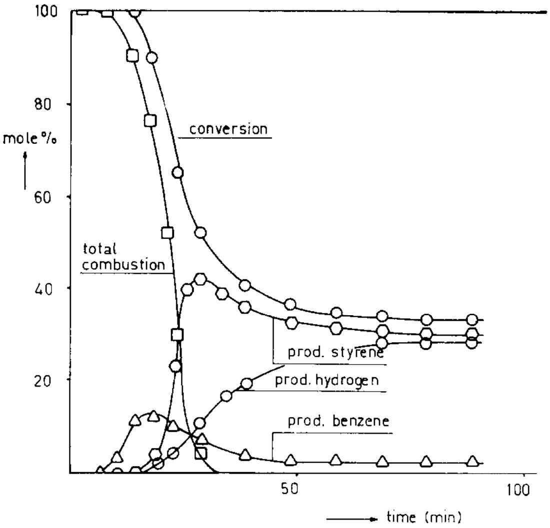

FIG. 4. Reduction of U_3O_8 to UO_2 with ethylbenzene: Reaction temp, 500°C; U_3O_8, 1.00 g; feed, 2.5 liters hr^{-1} N_2 and 0.327 mmol hr^{-1} ethylbenzene.

TABLE 3

RESULTS OF THE ETHYLBENZENE DEHYDROGENATION EXPERIMENTS AT 520°C OVER URANIUM OXIDE

Concn C_0 (mmol liter^{-1})	Contact time (sec)	Productivities (mole%) B	T	ST	Selectivity for styrene
	0.044	0.2	0.2	15.3	0.974
	0.058	0.2	0.2	18.4	0.977
0.0572	0.084	0.3	0.3	23.3	0.977
	0.167	0.6	0.6	38.4	0.974
	0.054	0.2	0.2	14.4	0.972
	0.058	0.2	0.2	17.2	0.974
0.0793	0.085	0.3	0.3	23.5	0.976
	0.166	0.5	0.4	37.9	0.977
	0.044	0.4	0.3	12.0	0.940
	0.058	0.3	0.7	14.1	0.934
0.1100[a]	0.084	1.1	0.4	16.7	0.918
	0.167	2.3	0.9	29.7	0.905
	0.045	0.1	0.2	11.6	0.970
	0.058	0.1	0.2	14.1	0.979
0.1233	0.085	0.2	0.2	17.6	0.978
	0.166	0.4	0.4	30.6	0.975
	0.045	0.1	0.2	9.4	0.969
	0.058	0.1	0.2	11.4	0.974
0.2028	0.085	0.1	0.2	15.7	0.983
	0.166	0.2	0.3	23.9	0.983

[a] During these runs the catalyst may not yet have been completely reduced and therefore oxidative benzene and toluene formation are possible.

TABLE 4

RESULTS OF THE CUMENE DEHYDROGENATION EXPERIMENTS AT 480°C OVER URANIUM OXIDE

Concn C_0 (mmol liter^{-1})	Contact time (sec)	Productivities (mole%) B	T	ST	α-MS	Selectivity for α-MS
	0.044	0.5	0.5	0.8	31.0	0.944
	0.059	0.6	0.5	0.6	40.3	0.959
0.0207	0.087	0.8	0.6	0.7	48.2	0.957
	0.172	1.3	0.9	0.8	66.3	0.957
	0.045	0.3	0.3	0.5	26.7	0.959
	0.059	0.4	0.4	0.9	31.7	0.952
0.0262	0.086	0.5	0.3	0.6	43.2	0.968
	0.170	1.0	0.7	0.6	60.8	0.964
	0.045	0.3	0.3	0.4	25.2	0.965
	0.059	0.4	0.3	0.6	33.2	0.964
0.0338	0.087	0.3	0.4	0.6	37.7	0.970
	0.171	0.7	0.4	0.5	55.7	0.973
	0.046	0.3	0.3	0.5	23.2	0.957
	0.060	0.3	0.3	0.6	24.8	0.955
0.0477	0.088	0.4	0.4	0.5	33.7	0.962
	0.172	0.5	0.4	0.5	49.5	0.972
	0.045	0.3	0.3	0.7	18.0	0.932
	0.059	0.2	0.2	0.5	22.6	0.957
0.0562	0.087	0.3	0.3	0.6	29.6	0.959
	0.172	0.5	0.4	0.5	44.4	0.970
	0.045	0.2	0.2	0.6	15.7	0.939
	0.060	0.2	0.2	0.6	19.1	0.949
0.0711	0.087	0.3	0.3	0.5	25.6	0.958
	0.172	0.5	0.4	0.5	39.9	0.968

REACTION KINETICS

Catalytic dehydrogenation reactions may be described with a model in which the reaction is assumed to be unimolecular on the catalytic surface (*5*, *15*). Calculations according to Hougen (*18*) and to Satterfield and Sherwood (*19*) have established that under our experimental conditions no limitations are to be expected by bulk gas phase or pore diffusion. Therefore we assume the surface reaction to be rate controlling. If we further assume that all components reach adsorption equilibrium the following rate equation corresponds to this model:

$$\frac{-dc_S}{d\tau} = \frac{\rho(k_1K_SC_S - k_{-1}K_UK_HC_UC_H)}{1 + \sum_i K_iC_i}. \qquad (1)$$

Because of the high reaction temperatures the adsorption constants of hydrogen and nitrogen should be considerably lower than the corresponding constants for hydrocarbons. Since no appreciable amounts of by-products were found, Eq. (1) can be approximated by

$$\frac{-dc}{d\tau} = \frac{k_1\rho K_SC - k_{-1}\rho K_UK_H(C_0 - C)^2}{1 + K_SC + K_U(C_0 - C)} \qquad (2)$$

$$= \frac{k_1\rho K_S\{C - [(C_0 - C)^2/K_{eq}]\}}{1 + K_SC + K_U(C_0 - C)}. \qquad (3)$$

The equilibrium constant K_{eq} for the ethylbenzene dehydrogenation was calculated from data given by Boundy and Boyer (*16*), and for the cumene dehydrogenation from data given by Emmett (*17*). From

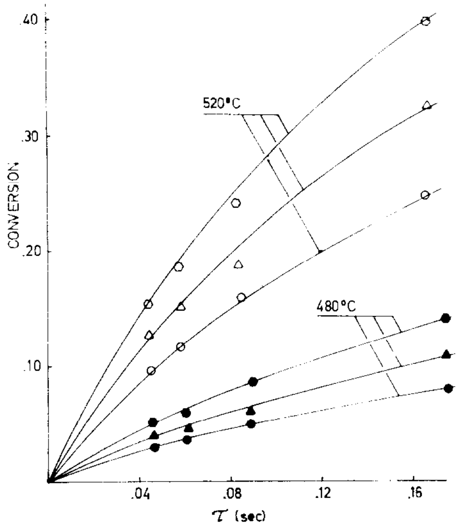

Fig. 5. Relation of ethylbenzene conversion and contact time at 520°C over uranium oxide (mmol liter^{-1}): (○) C_0 = 0.0572; (●) C_0 = 0.0603; (△) C_0 = 0.1100; (▲) C_0 = 0.1158; (○) C_0 = 0.2028; (●) C_0 = 0.2163.

Eq. (3) the concentration C was calculated numerically by the Runge-Kutta method as a function of τ, k_1, K_S and K_U. The values of k_1, K_S and K_U for the four reaction temperatures were determined by a numerical search procedure, minimizing the function.

$$f(k_1, K_S, K_U) = \sum_j (C_{m,j} - C_j)^2.$$

The values of k_1, K_S, K_U obtained from this equation are given in Table 5. The reaction rate curves, calculated from Eq. (3) with these values are drawn as solid lines in Figs. 5, 6, revealing a satisfactory agreement with the experimental data. From the Arrhenius plots for the surface reaction rate constants k_1, the energies of activation for the ethylbenzene and cumene dehydrogenations were found to be, respectively, 34 ± 1 and 27 ± 1 kcal mol^{-1}.

Discussion

Though reduced bismuth uranate gave good styrene yields, this compound is unsuitable as a dehydrogenation catalyst because under reaction conditions metallic bismuth is formed, which evaporates at reaction temperatures. On reoxidation only part of the metallic bismuth is converted to Bi_2UO_6, which may cause the erratic behavior of this catalyst mentioned earlier. Pure uranium dioxide is an active and stable catalyst for the dehydrogenation of ethylbenzene to styrene and cumene to α-methylstyrene. The kinetic model used was the most simple one that could describe our experimental data.

From the calculated results, shown in Table 5, we can conclude that the adsorp-

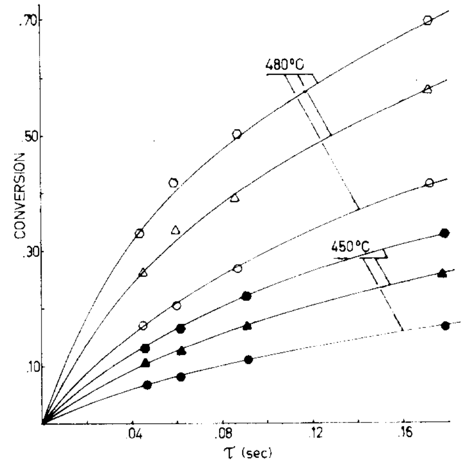

Fig. 6. Relation of cumene conversion and contact time over uranium oxide (mmol liter^{-1})· (○) C_0 = 0.0207; (●) C_0 = 0.0215; (△) C_0 = 0.0338; (▲) C_0 = 0.0352; (○) C_0 = 0.0711; (●) C_0 = 0.0741.

TABLE 5

Calculated Rate and Equilibrium Constants

Reaction temp (°C)	k_1 (mmol/g cat. sec)	K_S (liters/mmol)	K_U (liters/mmol)
	Ethylbenzene $\rightleftarrows$ styrene + H_2		
520	0.284×10^{-3}	6.3	48
500	0.150×10^{-3}	6.0	64
480	0.081×10^{-3}	6.7	157
460	0.053×10^{-3}	7.6	492
	Cumene $\rightleftarrows$ α-methylstyrene + H_2		
480	1.29×10^{-4}	75	320
465	0.83×10^{-4}	76	630
450	0.56×10^{-4}	55	800
435	0.43×10^{-4}	59	1870

tion of the saturated hydrocarbons is almost independent of the reaction temperature, but that the adsorption of the unsaturated products decreases strongly with increasing temperature. From Tables 3 and 4 and especially from similar experiments at lower reaction temperatures it can be concluded that the selectivity tends to improve when the contact time and hence the conversion increase. The same relation between conversion and selectivity is also found when the reaction temperature is varied. A preliminary conclusion could be that the unsaturated product formed has a negative influence on the production of by-products. We have indications that recycling of reactor product will effectively suppress by-product formation.

The proposed model may be used for preliminary design purposes but because no attention is given as yet to the formation of by-products, we intend to elaborate this model. Experiments for this purpose, also in a continuous stirred gas solid reactor, are under way. Special attention will be paid to the improvement of the selectivity at increasing conversions. Also the behavior of supported uranium oxide is under study and the results are promising.

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