

A MICROCATALYTIC TRACER EXPERIMENT

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Because of the rapid development of new analytical techniques and the increasing demands on students' time through expanded curricula, it has become necessary to streamline laboratory experiments to include as many of these techniques as possible in the shortest period of time. This report describes one of the experiments aimed at pursuing this goal in our senior chemical engineering laboratory and presents some results obtained by this year's students.

A large fraction of all industrial reactions are catalytic, and one of the most active areas in industrial research concerns the development of more active and selective catalysts for specific reactions. Although many of the early technological advances which revolutionized the petroleum industry before World War II were the result of empirical observations, the significant advances by such men as Sabatier,¹ Langmuir,² Taylor,³ Ipatieff,⁴ Emmett,⁵ and others have helped to change the application of catalysis from an art into a science.

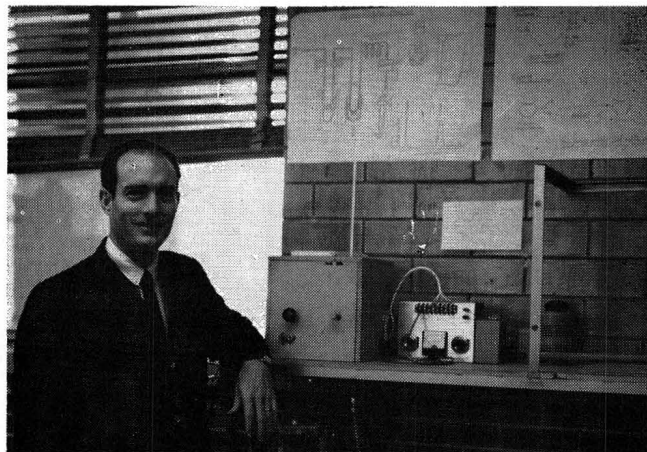
One of the standard catalytic activity tests in the petroleum industry involves the dealkylation of cumene (isopropylbenzene). This reaction seemed the logical choice for our studies over a standard silica-alumina cracking catalyst in a microcatalytic reactor for the following reasons:

It is essentially a "clean" reaction, i.e., the only significant products are propylene and benzene. There is little poisoning, which means the same catalyst can be used from day to day without reactivation. Reactant and product compounds are easily separated by GLC and are amenable to isotopic tracer investigations in a mass spectrometer. Cumene dealkylation has been used

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as a test reaction for diffusion studies⁶ and for investigations of active sites on zeolite catalysts.⁷ Cumene, an intermediate in the production of phenol and acetone, is an important commercial compound. Research involving this compound is currently under way at Rice. The entire experiment can be carried out in a reasonably short length of time.

EXPERIMENTAL

A microcatalytic reactor^{8,9} involves combination of a flow reactor with a gas chromatograph, Fig. 1. A helium carrier gas stream flowed continuously at 10 psig and about 100 cc/min through the reference side of a standard Gow-Mac thermal conductivity detector and then through a small packed catalyst bed containing a centered thermocouple well. Pulses of reactant could be injected by means of a 10 μ l hypodermic syringe through a rubber septum injection port A. The reactant was carried over the catalyst where it reacted, and the reaction products were swept immediately into the analyzing column, a six-foot coil of $\frac{1}{4}$ " copper tubing packed with silicone oil on firebrick. The separated products passed through the sample side of the Gow-Mac

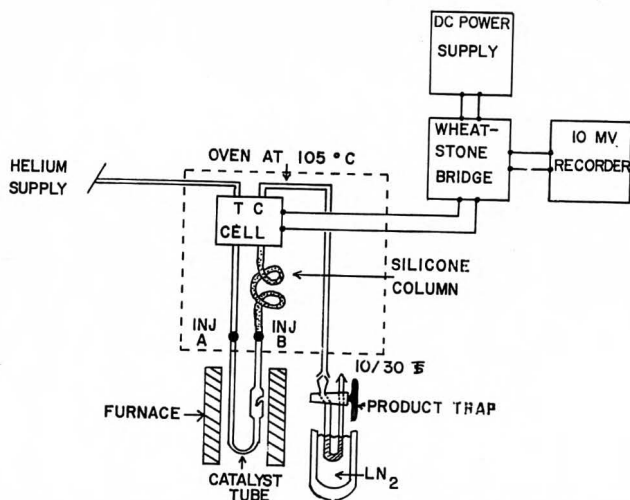


Fig. 1.—Schematic diagram of microcatalytic reactor and product traps.

detector where they caused an imbalance in a Wheatstone bridge which was recorded as a peak on a 10 mV strip chart recorder whose chart speed was 2 min/in. Calibration was effected for each compound by injection beyond the catalyst bed at injection port B. The injection ports, detector, and column were all enclosed in a transite box whose temperature was maintained near 115°C by means of a Variac which supplied power to the heating elements.

The separated products could be collected individually in a trap thermostated at -195°C (liquid nitrogen temperature) for subsequent analysis at low electron voltage in a CEC 21-104 medium resolution mass spectrometer. Helium was removed from the sample trap by evacuation at -195°C .

Pellets of commercial Houndry M-46 silica-alumina (12.5% alumina) were ground and collected between standard 20-60 mesh sieves to give particles which varied from 250 to 800 microns in diameter. Half a gram of this material was loosely packed to a depth of one cm between glass wool plugs in the 1.5 cm OD Pyrex reactor. The catalyst surface area was 270 m^2/g .

Initial activation was accomplished by heating the catalyst in flowing O_2 at 530°C for one hour to burn off carbonaceous residues, and the catalyst was then cooled in flowing helium to the 295-365°C reaction temperature range. Following this pretreatment, the catalyst retained a reproducible activity level for days without further reactivation. The temperature of the electrical resistance furnace around the reactor was controlled simply by a Variac.

RESULTS

The entire experiment was designed to cover three 3-hour laboratory periods. We have found it most effective when each group consisted of from three to six students. Our seniors were divided into five groups, with each group coming in on a different afternoon during the week to perform the same part of the experiment. This meant the whole experiment lasted three weeks. **Period I, Introduction** — During the first period, the objectives, techniques, and mathematical analysis of the experiment were described. Each student then practiced making benzene injections through injection port B until he obtained reproducible peaks on the GLC. Finally, each measured his peak areas with a planimeter until his measurements were reproducible. **Period II, Activation Energy** — A typical microcatalytic reaction spectrum is shown in Fig. 2. Besides the unde-

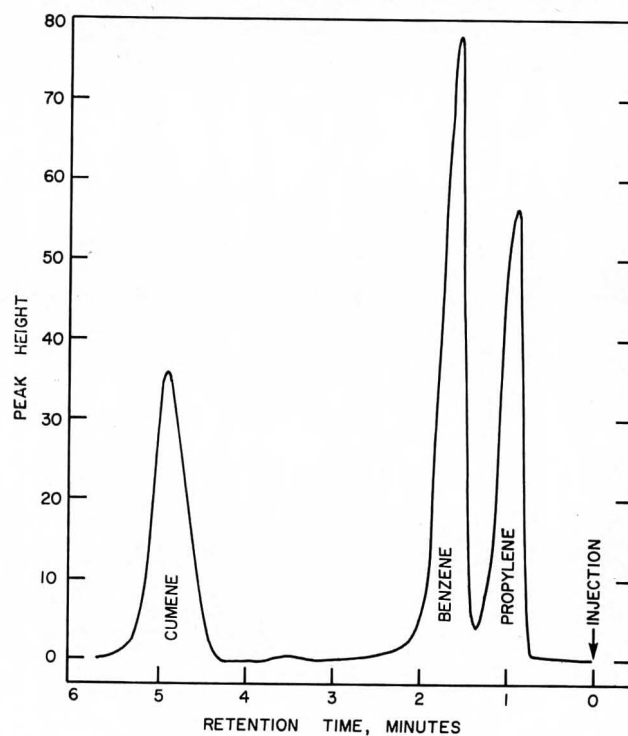


Fig. 2. — Typical chromatogram obtained from dealkylation of cumene over a silica-alumina catalyst in a microcatalytic reactor.

alkylated cumene, the only significant peaks observed were those of the products propylene and benzene. The small peak just before the cumene peak may represent a trace of the dehydrogenation product α -methylstyrene.

Conversions were determined from planimeter measurements of areas under the cumene (C) and benzene (B) peaks from the equation

$$\text{Fractional conversion} = B/(B+C) \quad (1)$$

The two compounds were assumed to have similar molar sensitivities.

Although the reaction is certainly much more complicated than this,^{6,10} for simplicity it was assumed to follow first order kinetics with no reverse reaction of products. Under the conditions used, equilibrium conver-

sion was greater than 99%, i.e., the reaction was essentially irreversible. The first order irreversible rate equation was transformed into one involving fractional conversion, x , and integrated to give

$$\ln \frac{1}{1-x} = A \exp(-E/RT)t \quad (2)$$

which can be written

$$\ln \left(\ln \frac{1}{1-x} \right) = -\frac{E}{RT} + \ln At \quad (3)$$

Since the pre-exponential factor A and the contact time t in the microcatalytic experiment are assumed to be essentially invariant with temperature, the activation energy E can be determined from the slope of a plot of $\ln \left(\ln \frac{1}{1-x} \right)$ versus $1/T$. Data from five sets of experiments on five different days by 13 seniors are shown collectively in Fig. 3; a least squares fit gives an apparent activation energy of 14.3 ± 0.9 kcal/mole. The sample size was $2 \mu\text{l}$ cumene at all temperatures in the region of 295 to 365°C .

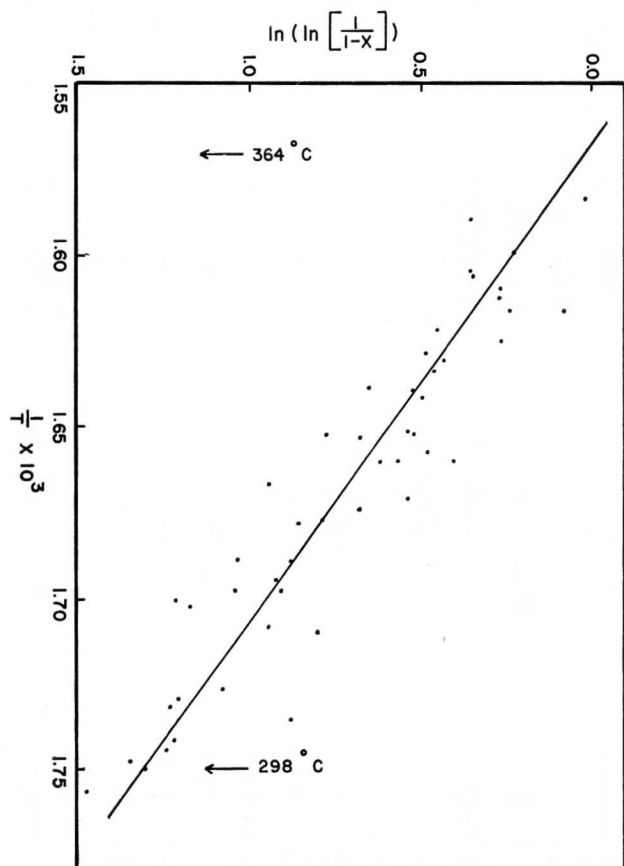


Fig. 3. — Compilation of data from 13 seniors showing temperature dependence of cumene dealkylation over silica-alumina in a microcatalytic reactor. The apparent Arrhenius activation energy is 14.3 kcal/mole.

Period III, Deuterium Isotopic Tracers — Measurements¹¹ by exchange with D_2 have shown that freshly activated silica-alumina contains about 4×10^{20} H atoms/g. These atoms have acidic properties and may provide Bronsted active sites on which the dealkylation reaction occurs. The purpose of this part of the experiment is to demonstrate participation of these atoms in several different

reactions which may occur.

When $2 \mu\text{l}$ pulses of benzene were passed over the catalyst at 340°C , there was apparently no chemical reaction, as only the benzene peak was observed in the GLC spectrum. Similarly, when perdeuterio benzene (C_6D_6) was injected, only one peak was observed. However, mass spectral analysis of that benzene peak showed that extensive exchange had occurred between the catalyst's H atoms and the hydrocarbon's D atoms.¹² Fig. 4

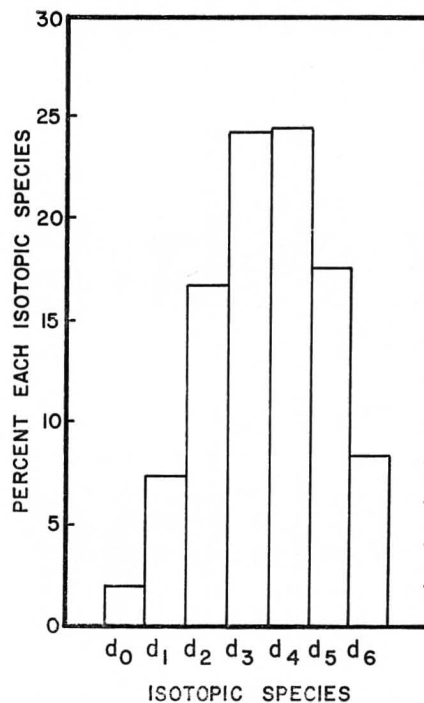


Fig. 4. — Deuterium distribution in benzene after exchange of a pulse of C_6D_6 with H atoms on the catalyst.

shows the relative amounts of product benzene molecules which contained from 0 to 6 D atoms. All peaks were corrected for naturally occurring C^{13} ; fragmentation involving loss of one or more H atoms was negligible under the low voltage mass spectrometer operating conditions used.

Seven more identical $2 \mu\text{l}$ pulses of C_6D_6 were then passed in succession every 10 minutes over the catalyst. The products were trapped and analyzed mass spectrally; the results are given in Table I. The last column showing the atoms exchanged/molecule was calculated from the equation

$$\text{Atoms Exchanged/Molecule} = \sum_{i=0}^6 (6-i) d_i / 100 \quad (4)$$

where d_i is the percent of molecules containing i deuterium atoms. As the pool of available H atoms on the surface became diluted with D atoms as a result of exchange with each successive pulse, the amount of measurable exchange decreased from pulse to pulse (see Fig. 5).

From the number of benzene molecules injected in each $2 \mu\text{l}$ pulse and the average number of atoms exchanged (or "titrated") per molecule, it was possible to determine the total number of surface H atoms which were exchanged in all eight pulses. Such a cumulative

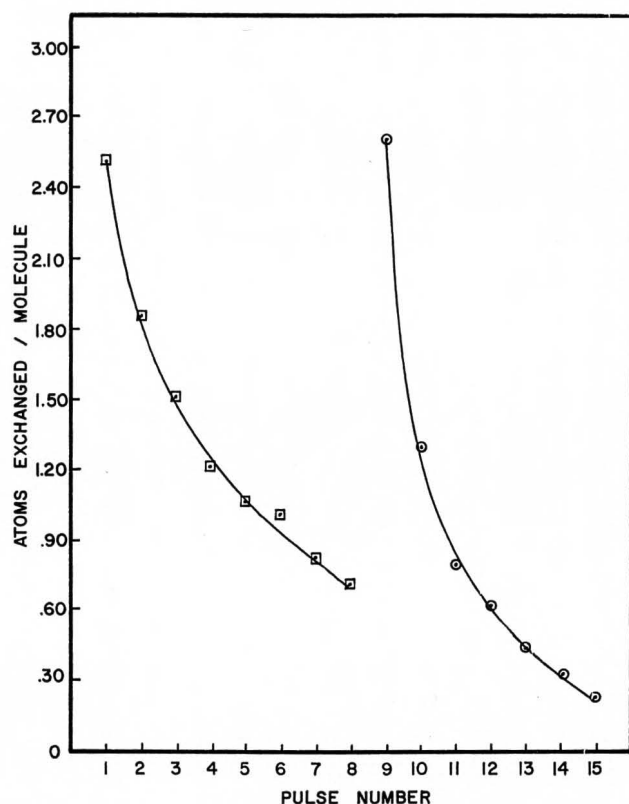


Fig. 5. — Average number of hydrogen atoms exchanged/molecule during successive passage of several pulses of benzene C_6D_6 and cumene over a silica-alumina catalyst in a microcatalyst reactor.

plot is shown in Fig. 6. A large fraction (about 75%) of the total H atoms originally present on the half gram sample underwent exchange during passage of these eight pulses of C_6D_6 .

With the catalyst now in a partially deuterated state, seven pulses of cumene were passed in succession over it at $340^\circ C$, and the conversion was constant at about 50% dealkylation. All three products were individually trapped and analyzed for pulse 9, but for the remaining pulses only the benzene peak was trapped and analyzed; the results are given in Table I. It is apparent from the results of pulse 9 that exchange was extensive in the undealkylated cumene as well as in the reaction products. In fact, to a rough approximation all the H atoms in all the hydrocarbons essentially equilibrated with the D atoms from the catalyst. For this to have been strictly true, the benzene and propylene (each has 6 hydrogen atoms) should have had the same number of D atoms/molecule, and cumene (12 hydrogen atoms) should have had double that amount using this assumption, and basing the calculation on the number of cumene molecules added and on the benzene mass spectral analysis, the cumulative number of D atoms recovered from the catalyst could be determined. The atoms exchanged/molecule were calculated from the equation

$$\text{Atoms Exchanged/Molecule} = \sum_{i=0}^6 id_i/100 \quad (5)$$

and the cumulative plot for pulses 9 through 15 is shown in Fig. 6. Most of the D atoms exchanged into the catalyst from the first eight C_6D_6 pulses were recovered in

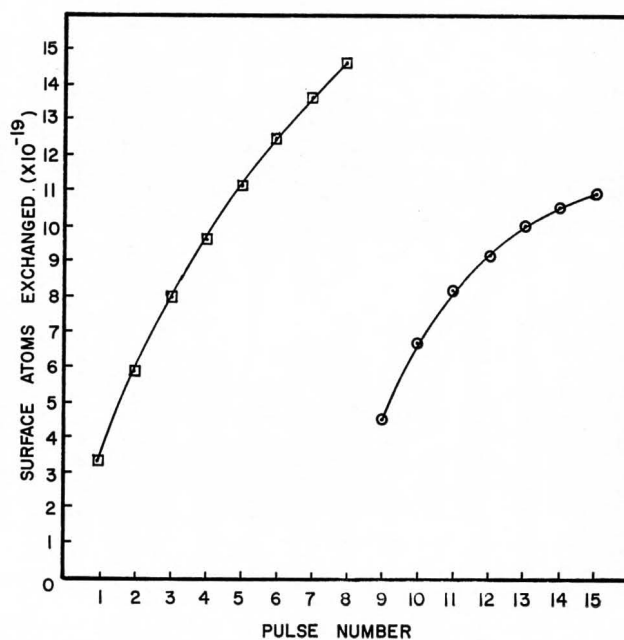


Fig. 6. — Cumulative of hydrogen atoms exchanged between catalyst and hydrocarbon during passage of successive pulses of benzene C_6D_6 and cumene over a silica-alumina catalyst in a microcatalytic reactor.

the hydrocarbon products during cumene dealkylation in the last seven pulses.

DISCUSSION

These microcatalytic tracer cumene dealkylation experiments over a silica-alumina catalyst are well suited for a senior chemical engineering laboratory. In a single integrated experiment involving three laboratory periods, the students are introduced to a wide range of concepts and techniques including catalysis, kinetics, gas chromatography, product trapping, vacuum systems, isotopic tracers, and mass spectrometry. None of the chemicals is very expensive, and the microcatalytic reactor (excluding the recorder and potentiometer) can be built for less than \$350. In our own department the mass spectrometer from the catalysis research laboratory was made available for these experiments. A research assistant was in charge of the mass spectral analyses, but the students themselves performed all other parts of the experiment.

The use of stable isotopic tracers has demonstrated that what appeared to be a relatively simple heterogeneous catalytic reaction in fact involves quite a complicated mechanism. This certainly invalidates the naive assumption of first order kinetics. Furthermore, since there was a temperature dependent peak broadening due to adsorption as each pulse was passed over the

Table I
Isotopic Composition of Products in Microcatalytic Tracer Experiments

Pulse No.	Injected	Measured	Isotopic Composition (%)										#D atoms molecule
			d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈	d ₉	
1	B, d ₆	B	1.7	7.3	16.7	24.1	24.4	17.6	8.2	-	-	-	2.522
2	B, d ₆	B	0.4	2.3	8.4	18.9	27.9	26.6	15.5	-	-	-	1.866
3	B, d ₆	B	0	0.9	4.7	14.2	26.9	32.6	20.7	-	-	-	1.523
4	B, d ₆	B	0	0.5	2.3	9.4	23.4	36.0	28.4	-	-	-	1.227
5	B, d ₆	B	0	0.1	1.5	7.1	21.0	37.2	33.1	-	-	-	1.070
6	B, d ₆	B	0	0	1.2	6.5	20.1	37.6	34.6	-	-	-	1.021
7	B, d ₆	B	0	0	0.6	4.0	16.0	37.3	42.1	-	-	-	0.837
8	B, d ₆	B	0	0	0.5	2.8	13.0	35.5	48.2	-	-	-	0.719
9	C, d ₀	P	1.2	9.6	22.6	29.5	23.4	11.0	2.7	-	-	-	3.081
		B	6.2	18.1	25.9	23.1	14.4	7.7	4.6	-	-	-	2.629
		C	3.8	13.8	22.6	21.8	15.3	9.4	6.1	4.2	2.1	0.9	3.235
10	C, d ₀	B	25.7	36.7	23.9	9.9	2.8	0.6	0.4	-	-	-	1.308
11	C, d ₀	B	43.8	37.0	15.1	3.6	0.5	0	0	-	-	-	0.800
12	C, d ₀	B	53.3	33.7	10.5	2.0	0.4	0.1	0	-	-	-	0.628
13	C, d ₀	B	63.3	29.5	6.5	0.7	0	0	0	-	-	-	0.446
14	C, d ₀	B	72.0	23.7	3.9	0.4	0	0	0	-	-	-	0.327
15	C, d ₀	B	79.1	18.8	2.1	0	0	0	0	-	-	-	0.230

catalyst, the assumption of constant contact time at various temperatures is also invalid. These two factors were mainly responsible for the apparent activation energy being much lower than that¹³ reported in the literature over similar catalysts in a steady state flow reactor.

Although microcatalytic reactors certainly are not the best suited systems for kinetic measurements, they are extremely useful for isotopic tracer studies for several reasons:

Tracer compounds are expensive, and only very small samples need to be used in this system. It is possible to study "initial" interactions between reactants and surface after only a relatively few hydrocarbon molecules have contacted the catalyst. The method is reasonably fast.

With very few changes, this system can be modified to study the reaction under steady state flow conditions. Kinetic comparison between the microcatalytic and steady state flow systems can be made to investigate the role of diffusion in the reaction. Furthermore, the GLC is sufficiently versatile that it can be used without modification for other analyses.

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