Supercritical Catalytic Dehydrogenation of Toluene

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Operation at above critical temperatures and pressures has received considerable attention (Paulaitis et al., 1983) as an extraction or separation process. This interest is based upon the greatly increased solubility and improved mass transfer rates obtained when solvents are at elevated temperatures and pressures (Subramanian and McHugh, 1986). Much less has been published on the effect of supercritical pressures and temperatures on reactions, particularly heterogeneous catalytic reactions. It has been demonstrated (Tilscher et al., 1981) that solid catalysts can be regenerated by treatment with a solvent at supercritical conditions. Also, Koll and Metzger (1978) have shown that increased yields of polysaccharides can be obtained by carrying out the decomposition of cellulose in a supercritical solvent (e.g., acetone) rather than by pyrolysis. We find no information on the effect of supercritical conditions on the rate of a heterogeneous catalytic reaction. This note provides some data on the PbO-catalyzed dehydrogenation of toluene to dibenzyl and stilbene.

The gas phase reactions of toluene at 813 to 873 K and atmospheric pressure with metal oxide catalysts have been reported in several patents. Montgomery et al. (1976) found stilbene as the primary product with dibenzyl and benzene as byproducts using a Pb/Al_2O_3 catalyst. The reactions were suggested to be of the oxidative dehydrogenation type with the oxygen supplied by the catalyst. Best results were obtained with catalysts containing large amounts of PbO (up to 20 wt. %). Our objective was to find out if toluene would react at the milder temperature but higher pressure corresponding to close to critical conditions (for toluene $T_c = 592$ K, $P_c = 4.23 \times 10^3$ kPa).

Experimental Procedure

Figure 1 is a diagram of the apparatus. The essential feature is a stainless steel tubular reactor (2.9×10^{-2} m ID) in which was placed about 0.01 kg of catalyst particles. A nitrogen cylinder provided the pressure for flowing toluene through a preheater coil wound around the reactor, and down through the catalyst bed. The reactor assembly was surrounded by an electric heater. After pressure and temperature reduction, the effluent stream from the reactor was continuously analyzed in a Perkin-Elmer Lambda 4B UV/VIS spectrophotometer. Complete details of the apparatus are available elsewhere (Triday, 1986).

To operate the equipment, the system was first pressurized, then the toluene flow started and the furnace turned on. All data were taken at a flow rate of 3.33×10^{-7} m^3/s (at 101.3 kPa and 298 K). Concentrations in the effluent were calculated from the absorbance measured after steady state was attained.

The catalyst was prepared by degassing α-alumina particles (properties given in Table 1) in vacuum for two hours, soaking in aqueous $PbNO_3$ solution, drying at 473 K for 24 h, and calcining at 873 K for 2 h. The PbO content of the calcined material was 1.0%. Particles between 14 and 96 Tyler mesh (average particle dia. = 1.097×10^{-3} m) were used to pack the reactor.

The absorbance measurements were converted to concentration by assuming that the only product was dibenzyl for the runs at 643 K ($T_r = 1.09$). A calibration curve of absorbance vs. concentration was measured for solutions of dibenzyl in pure toluene at a wavelength of 360 nm. This curve was used with the absorbance of the reactor effluent to establish the dibenzyl concentration. Concentrations were not determined for the runs at 453 K because the reactor effluent contains other products than stilbene. Toluene used for the runs and for calibration was certified to be 99.99% pure.

Results

A typical curve of absorbance (at 360 nm) vs. time is shown in Figure 2 for a run at 4.76×10^3 kPa ($P_r = 1.13$) and 643 K ($T_r = 1.09$). The large peak at low times was always observed and is probably due to the considerable change in physical properties, particularly density, that occurred during the dynamic heating-up period before the constant temperature was reached (i.e., as the temperature increased through T_c). To evaluate the concentration of dibenzyl, samples of effluent were collected at long times where steady state was approached. These samples were then analyzed in the spectrophotometer to obtain an absorbance

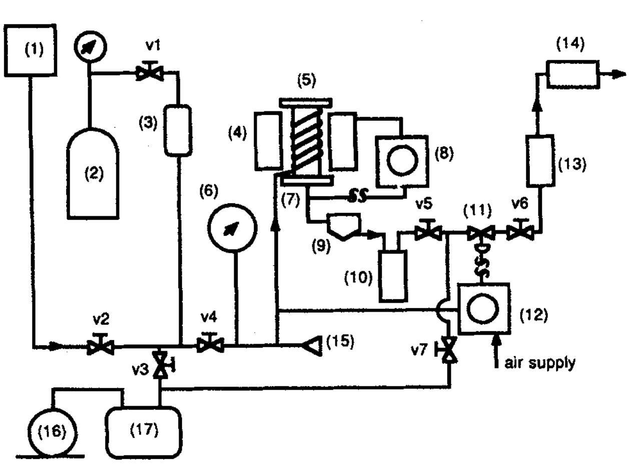

Figure 1. Experimental apparatus.

1. Supply tank
2. Nitrogen cylinder
3. Feed tank
4. Furnace
5. Reactor
6. Gauge
7. Thermocouple
8. Temperature controller
9. Filter
10. Cooler
11. Control valve
12. Pressure controller
13. Rotameter
14. Spectrophotometer
15. Rupture disk
16. Mechanical vacuum pump
17. Surge tank

v1–v7. Shutoff valves

Table 1. Properties of Catalyst Support Al_2O_3*

Surface area (N_2 adsorption), m^2/g	165
Pore volume, m^3/kg	0.33×10^{-3}
Avg. pore radius, Å	60
Solid density, kg/m^3	3.07×10^3
Particle density, kg/m^3	1.53×10^3
Bulk density, kg/m^3	0.79×10^3
Avg. radius of particle, m	6.27×10^{-5}
Porosity of particle, β	0.503

*Morita and Smith (1978)

vs. wavelength scan. A scan of a sample collected after 4,800 s for the run shown in Figure 2 is shown in Figure 3. This figure also shows a scan of a solution in toluene containing 4.5 g of pure dibenzyl per 100 cm^3 solution (4.5 kg/m^3 solution). The similarity of the two curves suggests that the product is primarily dibenzyl. The peak at 360 nm is characteristic of the spectrum for dibenzyl and the absorbance at this wavelength was used to evaluate the concentration of the reactor effluent. No doubt small amounts of other products were present in the solution. Particularly the absorbance at 300 nm suggests the presence of stilbene. The high absorbance in the region of 280–300 nm does

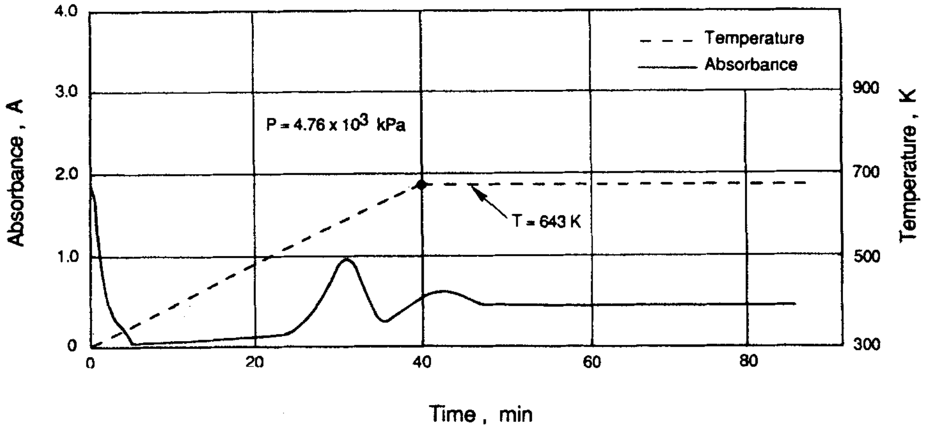

Figure 2. Absorbance curve of reactor effluent at 360 nm.
Run 9: $T = 643$ K, $P = 4.76 \times 10^3$ kPa

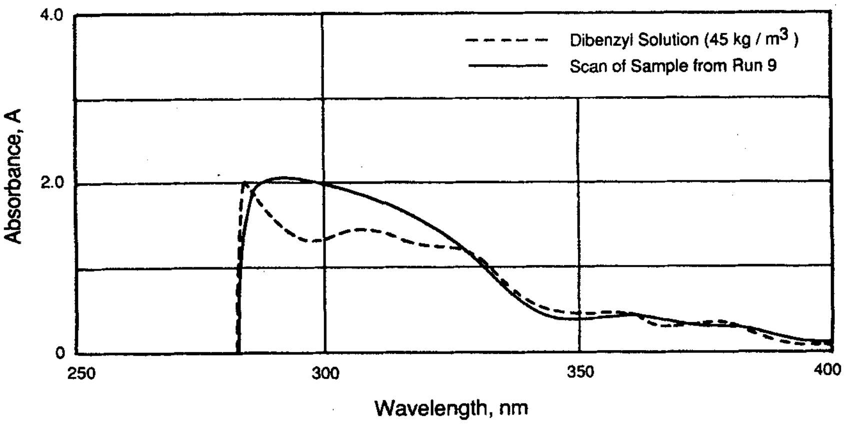

Figure 3. Scan of product sample taken at 4,200 s.
Run 9: $T = 643$ K, $P = 4.76 \times 10^3$ kPa

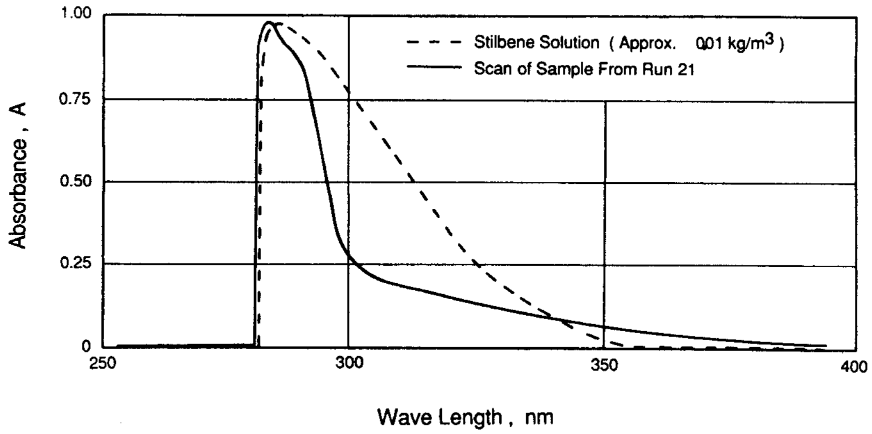

Figure 4. Scan of product sample taken at 3,600 s.
Run 21: $T = 453$ K, $P = 4.76 \times 10^3$ kPa

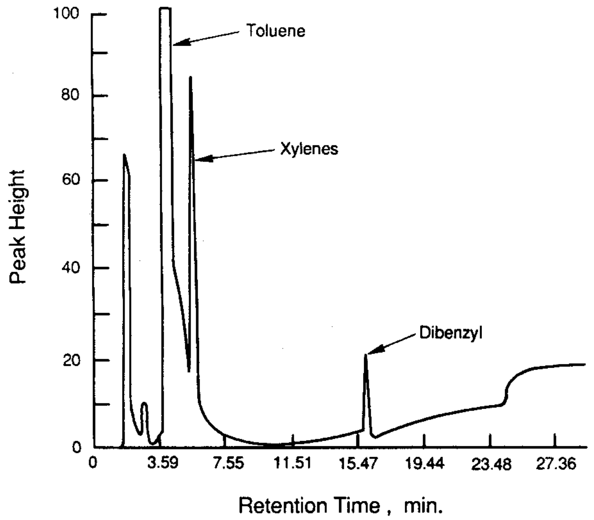

Figure 5. Chromatograph of sample of reactor effluent.
Run 9: $T = 643$ K, $P = 4.76 \times 10^3$ kPa

Table 2. Reproducibility of the Data

Temp. K	Press. kPa × 10^3	Wavelength nm	Absorbance	Dibenzyl Conc. kg/m^3
643	1.72	360	0.35	21
643	1.72	360	0.30	19
643	4.76	360	0.87	42
643	4.76	360	0.72	36
643	4.76	360	0.97	46
453	4.76	300	0.12	—
453	4.76	300	0.11	—

not suggest a high concentration of stilbene since its absorptivity is very high in this region.

Figure 4 is a scan of a sample collected at $t = 4{,}200$ s for a run at 4.76×10^3 kPa and 453 K. The spectrum of a very dilute solution (approx. 0.01 kg/m^3) of stilbene in toluene is also shown. The two curves are similar in the 250–300 nm range, but there are no dibenzyl peaks at 360 nm or at 380 and 325 nm. These qualitative analyses suggest that dibenzyl is the primary product for the runs at the supercritical temperature (643 K) while mostly stilbene is produced at 453 K.

Further evidence for the production of dibenzyl at 643 K was

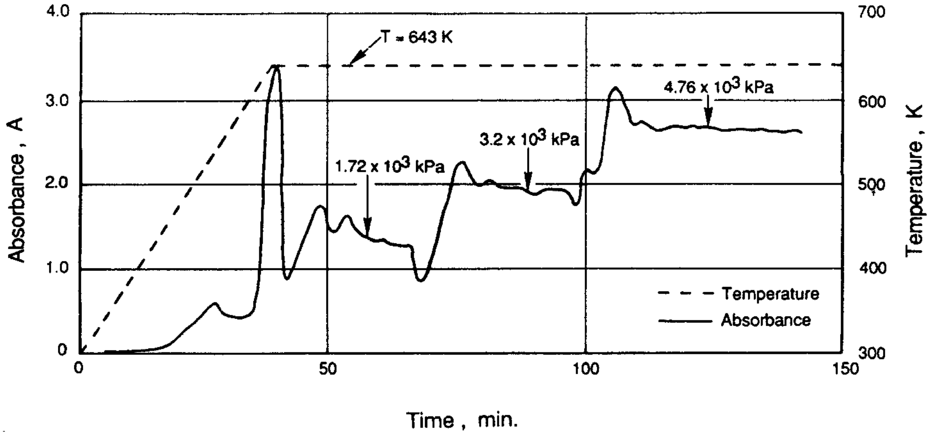

Figure 6. Effect of pressure on absorbance of reactor effluent at 300 nm.

Table 3. Rates of Production of Dibenzyl

Press. kPa × 10^3	Dibenzyl Conc. kg/m^3	r (kmol/s · kg cat) × 10^6
1.72	21	3.86
3.14	29	5.95
4.76	46	8.20

obtained from gas chromatographic analysis. Figure 5 shows the chromatograph for a sample of reactor effluent from a run at 4.76 × 10^3 kPa and 643 K. The peak for dibenzyl is apparent at a retention time of about 960 s (using a 30 m capillary column [DB1] operated from 323 to 523 K with a 0.1 K rise per second). The chromatograph for the toluene fed to the reactor was the same as that in Figure 5 except for the dibenzyl peak. Stilbene could not be separated since its retention time was essentially the same as that for toluene.

For operating times up to 7 h, reasonably reproducible results were obtained. This is seen by the absorbances for multiple runs given in Table 2 for different temperatures and pressures. After about 7 h the catalyst particles become black, and after a longer period of operation appreciable amounts of carbonaceous material were observed on the inside wall of the reactor.

To see if supercritical conditions affected the rate of reaction, continuous runs were made at 643 K, increasing the pressure after steady state was reached from 1.72 × 10^3 kPa ($P_r = 0.41$), to 3.20 × 10^3 kPa ($P_r = 0.76$), and to 4.76 × 10^3 kPa ($P_r = 1.13$). Figure 6 shows that the absorbance increased for each pressure, although unavoidable variations in operating conditions caused extraneous peaks in the curve. The first large peak is due to the temperature passing through the critical value; the subsequent peaks and dips are primarily the result of changing the pressure. Pressure changes always caused an immediate change in flow, which in turn resulted in temporary temperature fluctuations. When steady state was again approached, the temperature could be held constant within ±1 K. Despite the fluctuations, the data show that the absorbance increased with pressure; average values are listed in Table 3. Shown also are rates of production of dibenzyl estimated from the differential reactor equation:

$$r = \frac{Q(C_e - O)_b}{m_c} \tag{1}$$

Scans of samples of the reactor effluent taken during operation at different pressures were essentially identical. Thus, the product composition did not change with pressure, in contrast to the results at the two temperatures.

Conclusions

In the present work we have investigated the PbO-catalyzed dehydrogenation of toluene at subcritical and supercritical temperatures and pressures. The results show that the rate of producing dibenzyl more than doubled when the pressure was increased from a subcritical to a supercritical level ($P_r = 1.13$).

This occurred at a supercritical temperature, 643 K, considerably lower than the temperatures at which the reaction has been studied in the gas phase at atmospheric pressure with the same catalyst. Also, it is interesting that the reaction product included considerable stilbene when the temperature was lowered to 453 K at the same supercritical pressure.

Acknowledgment

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Notation

A = absorbance
C_b = dibenzyl concentration, kmol/m^3; $(C_e)_b$ refers to reactor effluent
m_c = mass of catalyst in reactor, kg
P = pressure, kPa
P_c = critical pressure
P_r = reduced pressure
Q = volumetric flow rate at 101.3 kPa and 298 K, m^3/s
r = rate of production of dibenzyl, kmol/s · kg cat
T = temperature, K
T_c = critical temperature
T_r = reduced temperature

Literature Cited

Koll, P., and J. Metzger, "Thermal Degradation of Cellulose and Chitin in Supercritical Acetone," *Angew. Chem., Int. Ed.*, **17**, 754 (1978).

Montgomery, P. D., C. Couer, R. Moore, and W. R. Knox, "Production of Stilbene and Styrene," U.S. Pat. 3,965,206 (1976).

Morita, S., and J. M. Smith, "Mass Transfer and Contacting Efficiency in a Trickle-Bed Reactor," *Ind. Eng. Chem. Fundam.*, **17**, 113 (1978).

Paulaitis, M. E., V. J. Krukonis, R. T. Kurnik, and R. C. Reid, "Supercritical Fluid Extraction," *Rev. Chem. Eng.*, **1**, 179 (1983).

Subramanian, B., and M. A. McHugh, "Reactions in Supercritical Fluids—A Review," *Ind. Eng. Chem. Process. Des. Dev.*, **25**, 1 (1986).

Tilscher, W., H. Wolf, and J. Schelckskorn, "A Mild and Effective Method for the Reactivation or Maintenance of Activity of Heterogeneous Catalyst," *Angew. Chem., Int. Ed.*, **20**, 892 (1981).

Triday, J., "Supercritical Extraction of Kerogen from Oil Shale," Ph.D. Thesis, Univ. California, Davis (Feb., 1987).

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