A Kinetic Study on the Hydrogenolytic Dealkylation of Toluene with High Pressure Flow Reactor

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Summary

A kinetic analysis was carried out, with a continuous flow reactor, for demethylation of toluene to yield benzene under pressures ranging from 10 to 50 atm and at temperatures from approximately 580° to 680°C, while maintaining the hydrogen to toluene mole ratio constant at 4.

The 1.5-order rate was confirmed in agreement with those of previous works conducted by Silsby⁷⁾ and Tokuhisa⁴⁾, and the reaction rate is expressed as follows:

$r = 3.55 \times 10^5 \exp(-54,500/RT) (p_H^{0.5})(p_T^{1.5})$. And contact time is written as,

$$\theta = \frac{0.0281}{3.55 \times 10^5 \exp(-54,500/RT)} \frac{1}{\sqrt{p}} \frac{1}{T} \sqrt{\frac{1+a}{a-1}} \cdot \log \left\{ \frac{\sqrt{a-x} + \sqrt{a-1}}{\sqrt{a-x} - \sqrt{a-1}} \frac{\sqrt{a} - \sqrt{a-1}}{\sqrt{a} + \sqrt{a-1}} \right\}$$

Introduction

An industrial significance has been given to the demethylation reaction of toluene to produce benzene, because the successful application of reforming and extraction techniques to naphtha has brought about an ample production of toluene, in quantity 2 to 3 times that of benzene produced. Also the reaction is of interest from the standpoint of chemical kinetics.

A number of papers have been already published on this theme, and in Japan also, several works have recently been reported by Ando^{1), 2)}, Morikawa³⁾ and Tokuhisa^{4), 5)}. Ando^{1), 2)} has studied the thermal dealkylation of toluene and xylene in the presence of hydrogen at the experimental conditions: 670~830°C/5~20 kg/cm², and obtained a single pass conversion to benzene of about 72% at the optimum set of processing variables: 770°C/16 kg/cm². Morikawa³⁾ has carried out some investigation on the catalytic reaction in the presence of hydrogen in a somewhat lower temperature range and at atmospheric pressure, and found a nickel-

silica catalyst suitable.

On the kinetic study of this homogeneous reaction, a patent⁶⁾, covering the range of temperature: 1,100~1,800°F, pressure range: 400~1,000 lb/in², describes the rate equation of pseudo 1.0 order. Silsby⁷⁾ has tried to determine the kinetics and found the order of reaction to be 1.5 and the activation energy to be 50 ± 5 kcal/mol at 500~600°C/250 atm and at 700~950°/atmospheric pressure. But he found the rate constants, calculated from the experimental data⁸⁾ obtained at 540~660°C/100 atm, on the basis of 1.5 order reaction, to be lower than he had expected, and he discussed the cause for this discrepancy. Tokuhisa⁴⁾ has made two sets of experiments, with both static and flow reactors under atmospheric pressure, and obtained the order of 1.5 and the activation energy of 47 and 49.8 kcal/mol, respectively.

In regard to these previous works, we attempted to obtain more detailed kinetic data for this reaction in the pressure range from atmospheric to 50 atm and at temperatures from about 580° to 680°C, which conditions, we thought, might be most favorable for commercial processing.

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Equipment and Procedure

Experiments were carried out in a small scale flow system illustrated in Fig. 1. The liquid feed was pumped into a 25 Cr-20 Ni S.S. reactor tube, 25 mm in internal diameter and 880 mm long, where it was combined with hydrogen from a cylinder. The central zone of the reactor, 500 mm in length, was filled with 3×3 mm Raschig rings made of the same material as the reactor tube. An electrically heated furnace surrounding the reactor, was controlled automatically to $\pm 2^\circ\text{C}$. A movable thermocouple inserted in the thermowell, located at the center of the reactor, permitted temperature measurements along the reaction zone.

The reactants entered from top and passed through the reactor. The products were cooled by a water condenser and then run into a gas separator, where the liquid product was collected. The separated gas was released through a needle valve, then passed through a trap immersed in a dry ice-methanol bath and, finally, a wet test meter.

The liquid product was combined with the condensate from the trap, and distilled to remove a trace amount of polymerized product. The distillate was submitted to the gaschromatographic

analysis under the following conditions:

Column packing: 40 g/100 g of di-*n*-nonyl-phthalate on fire-brick (40 mesh)
 Column size: 1/4 inch by 6 feet copper tube
 Carrier gas: Helium
 Flow rate: 25 cc/min
 Column temperature: 108°C

Molar percentage composition was calculated by comparing the area under each peak corresponding to benzene and toluene using the calibration factor obtained from the preliminary analyses of benzene-toluene mixtures of known compositions. This method is accurate to about $\pm 0.5\%$ of the amount present.

Materials

Toluene was of nitration grade obtained from the Udex unit of Mitsubishi Oil Co., Ltd., and except for drying, it was used without further purification. Commercial cylinder hydrogen was used. A trace amount of oxygen contained was removed over a Baker Deoxo catalyst, and dried over silica gel adsorbent.

Benzene and toluene used as analytical standards were also of nitration grade obtained from the

Fig. 1 Schematic Diagram of High Pressure Flow Unit.

same plant.

	Benzene	Toluene
Density, 15/4°C	0.8817	0.8702
Freezing Pt., °C	5.30	—
n_d^{20}	1.5010	1.4962

Temperature Measurements and Average Effective Temperature

When there exists a certain temperature distribution in an experimental reactor, it is proposed⁹ that average effective temperature and equivalent reactor volume may be used.

The equivalent reactor volumes of Run No. 26 to Run No. 40, where the pressure was varied, were calculated by assuming the average effective temperature, preferentially, as 650°C and the activation energy of this reaction as 54 kcal/mol. Thus, we obtained the equivalent reactor volume, $V_e = 71.7 \text{ cm}^3$.

The average effective temperatures from Run No. 41 to Run No. 53, where the reaction temperature was varied, were calculated in the same manner, while the equivalent reactor length was fixed at 45 cm.

Experimental Results

In a series of runs (Run No. 26–40), demethylation of toluene was investigated for its order of reaction over a wide pressure range, i.e., from 10 atm to 50 atm, while the reaction temperature was held constant. On the other series of runs (Run No. 41–53), an investigation was made on the effect of temperature on the demethylation of toluene, that is, the temperature was varied from 585° to 686°C (T_{av}) at a constant pressure of 40 atm. The hydrogen to hydrocarbon mole ratio was maintained at about 4 throughout these two series.

Tables 1 and 2 give the summarized experimental results. The reaction temperatures in the second column indicate those at the central point of the reaction zone, and the average effective temperatures (in the third column) used in this kinetic study were calculated by the above-mentioned method. In the fourth column are given the contact times. The lower the reaction pressure, the shorter is the contact time for a given feed rate; so the feed rates were lowered in order to secure nearly the same contact times for the runs

Table 1 Summary of Demethylation of Toluene: Effect of Pressure

Run Nos.	Reaction	Temperature	Contact time θ , sec.	Total Pressure P , atm.	H_2 /Toluene Mole Ratio, a	Conversion, x	Liquid Recovery, mol %	Rate Constant $k_{1.5 \times 10^3}$, mol/cc. sec. atm. ^{1.5}
	Central Point, °C	T_{av} , °K						
40	650	923	9.6	10.7	3.61	0.119	95.3	53
31	"	"	9.9	11.6	3.70	0.097	101.7	36
26	"	"	20.0	23.1	4.00	0.324	101.3	58
36	"	"	14.2	25.7	3.62	0.196	98.2	44
28	"	"	22.1	31.0	4.21	0.353	99.2	56
35	"	"	16.4	34.8	3.58	0.236	90.7	36
34	"	"	18.8	40.6	3.70	0.272	100.4	39
27	"	"	19.9	40.7	3.45	0.348	98.1	59
33	"	"	18.9	45.0	3.51	0.270	104.5	37
39	"	"	19.9	49.4	3.72	0.290	92.3	41
32	"	"	17.0	49.5	3.97	0.270	98.5	37

Table 2 Summary of Demethylation of Toluene: Effect of Temperature

Run Nos.	Reaction	Temperature	Contact time θ , sec.	Total Pressure P , atm.	H_2 /Toluene Mole Ratio, a	Conversion, x	Liquid Recovery, mol %	Rate Constant $k_{1.5 \times 10^3}$, mol/cc. sec. atm. ^{1.5}
	Central Point, °C	T_{av} , °K						
41	593	858	28.7	40.7	4.05	0.042	97.5	3.8
42	610	868	29.4	40.7	3.75	0.061	97.1	7.1
43	625	882	30.2	40.4	4.04	0.124	98.2	10
44	640	896	31.5	40.7	3.53	0.192	97.8	16
53	650	905	31.4	40.6	3.70	0.272	100.4	24
48	660	915	30.8	39.7	3.35	0.362	98.3	35
45	664	918	32.6	39.7	3.19	0.391	96.2	38
46	680	933	37.1	40.7	2.80	0.600	93.1	63
47	690	942	37.5	39.7	2.77	0.709	99.3	86
50	690	942	34.6	39.7	3.04	0.682	92.9	83
51	700	951	23.8	40.2	3.52	0.726	98.9	139
52	709	959	27.3	39.7	2.86	0.785	87.9	142

in the same series, except for Run Nos. 30 and 40, which were made at the lowest pressures, and smooth operation of the pump was difficult. In the fifth, sixth and seventh columns are given the total pressures, hydrogen to toluene mole ratios and molar fractions of benzene in the liquid product, respectively. In the eighth column, liquid recoveries are shown by mol % on the fed toluene. Each run was continued for 1.5 hours at the stationary conditions to obtain a sufficient quantity of sample for analysis.

Kinetic Consideration and Discussion

Generally speaking, the kinetic treatment might be difficult in such a high temperature range as indicated above because of the accompanying side reactions such as cracking to produce carbonaceous deposits, condensation to polycyclic products etc. By rendering special consideration in the experimental technique, these side-reactions could be suppressed to a negligible extent, and the product was confined almost exclusively to benzene and methane, as was confirmed by gas and liquid analyses. It was demonstrated by Tokuhisa⁵⁾ that the reverse reaction—methylation of benzene to toluene—was negligible even though the partial presence of methane was 3 times that of hydrogen. In this case, toluene was principally decomposed according to the stoichiometric equation as follows:

$$1-x \quad a-x \quad x \quad p_H = P \frac{a-x}{1+a} \quad (2)$$

Assuming 1.5 order rate for this reaction, as is shown by Silsby and Tokuhisa, the reaction rate is expressed by,

$$\begin{aligned} r &= F_T \frac{dx}{dV_e} = k_{1.5} p_T^{1.5} p_H^{0.5} \\ &= k_{1.5} P^{1.5} \frac{(1-x)(a-x)^{1.5}}{(1+a)^{1.5}} \end{aligned} \quad (3)$$

And the rate constant is given by,

$$\begin{aligned} k_{1.5} &= \frac{0.0281}{T_{av} \theta \sqrt{P}} \sqrt{\frac{1-a}{a-1}} \\ &\log \left\{ \frac{\sqrt{a-x} + \sqrt{a-1}}{\sqrt{a-x} - \sqrt{a-1}} \cdot \frac{1 - \sqrt{a-x} + \sqrt{a-1}}{1 + \sqrt{a-x} + \sqrt{a-1}} \right\} \end{aligned} \quad (4)$$

where,

$$\theta = \frac{V_r}{F \cdot 22,400 \frac{T_{av}}{273} \frac{1}{P}} \quad (5)$$

Fig. 2 Arrhenius Plot of Demethylation of Toluene.

The results of rate constant $k_{1.5}$, which indicate a fairly good constancy (mean deviation: $\pm 9 \times 10^{-5}$) independent of reaction pressure as shown in the last column of Table 1, were calculated using Equation (4).

The rate constant $k_{1.5}$ over a temperature range from 585° to 686°C was calculated in the same manner, and the Arrhenius plot is shown in Fig. 2, and the activation energy was determined as 54,500 cal/mol. This value is in fairly good agreement, within the experimental error, with 49.8 kcal/mol by Tokuhisa⁴⁾ and 50 ± 5 kcal/mol by Silsby⁷⁾ and is in better agreement with 55 kcal/mol, which Silsby assumed to be quite reasonable. The frequency factor was also determined; it was found to be 3.55×10^5 mol/cc sec atm^{1.5}, which was comparable to Tokuhisa's value 0.94×10^5 mol/cc sec atm^{1.5} and Silsby's $1 \times 10^{10.5} \pm 1$ l^{0.5}/mol^{0.5} sec. The over-all reaction rate is then expressed as follows;

$$r = 3.55 \times 10^5 \exp(-54,500/RT) (p_H^{0.5}) (p_T^{1.5}). \quad (6)$$

And the contact time to give a target conversion x is calculated by the equation below:

$$\theta = \frac{0.0281}{3.55 \times 10^5 \exp(-54,500/RT)} \cdot \frac{1}{\sqrt{p}} \cdot \frac{1}{T} \sqrt{\frac{1+a}{a-1}} \cdot \log \left\{ \frac{\sqrt{a-x} + \sqrt{a-1}}{\sqrt{a-x} - \sqrt{a-1}} \right\} \cdot \frac{\sqrt{a} - \sqrt{a-1}}{\sqrt{a} + \sqrt{a-1}} \quad (7)$$

In the course of our experiment, it was experienced that, when the reaction temperature exceeded approx. 700°C, carbonaceous materials deposited on the packings in the reactor and clogged it. This difficulty might pose a serious problem with regard to developing the process commercially. To avoid it a careful search was made for a satisfactory reactor device, and a continuous run, extending over a half a month was made on the bench scale pilot plant in the reaction temperature range of 700~710°C without any trouble caused by carbon deposition. Equation (7) was found to apply satisfactorily to the actual operating results which encouraged commercialization of the process.

The benzene produced from this process meets the ASTM specifications for nitration grade quality. This means that it contains no impurities such as olefins, paraffins and naphthenes, and this fact suggests that the process is rather simple and straight-forward, and its commercialization is feasible on which further investigation is now being continued.

Nomenclatures

- A = frequency factor, mol/cc sec atm^{1.5}
 a = hydrogen to toluene mole ratio, mol/mol
 E = activation energy, cal/mol
 F = total feed rate, mol/sec = $F_T(1+a)$
 F_T = toluene feed rate, mol/sec
 $k_{1.5}$ = rate constant for one and a half order, mol/cc sec. atm^{1.5}
 P = total pressure, atm

- P_H = partial pressure of hydrogen, atm
 p_T = partial pressure of toluene, atm
 R = gas constant, 1.987 cal/°K mol
 r = reaction rate, mol/cc sec
 T = temperature, °K
 T_{av} = average effective temperature, °K
 V_e = equivalent reactor volume, cc
 x = conversion, mole fraction
 θ = contact time, sec

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References

- 1) Andō S. and Sada M., *11th Annual Meeting of J.C.S.*, Tokyo, April 1958.
- 2) id., *Meeting of Japan Fuel Society*, Tokyo, Sept. 1958.
- 3) Morikawa K. and Nozaki F., *Autumn Meeting of J.C.S.*, Tokyo, Nov. 1958.
- 4) Tokuhisa H., Amano A. and Matsui, H., *11th Annual Meeting of J.C.S.*, Tokyo, April 1958.
- 5) Tokuhisa H., Amano A. and Masamune S., *Meeting of J.C.S.*, Morioka, Oct. 1958.
- 6) Standard Oil Development Co., *B.P.* 712,440.
- 7) Silsby R.I. and Sawyer E.W., *J. Appl. Chem.*, **6**, 347 (1956).
- 8) Betts, W.D., Popper F. and Silsby R.I., *ibid.*, **7**, 497 (1957).
- 9) *Chemical Process Principle* (Hougen, O.A., & Watson, K.M., 1950, John Wiley & Sons Inc.) p. 884.