Mechanism of Thermal Hydrogenolysis of Toluene*

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Summary: Kinetic parameters of a number of possible elementary reactions involved in the thermal hydrogenolysis of toluene are evaluated based on the bulk of kinetic and thermodynamic informations. More important elementary reactions are thus selected resulting in the following formulation to describe main scheme of the hydrogenolysis: $C_6H_5 \cdot CH_3 \rightleftharpoons C_6H_5 \cdot CH_2 + H$, $H + C_6H_5 \cdot CH_3 \rightleftharpoons H_2 + C_6H_5 \cdot CH_2$, $H + C_6H_5 \cdot CH_3 \longrightarrow C_6H_6 + CH_3$, $CH_3 + H_2 \longrightarrow CH_4 + H$, and $CH_3 + C_6H_5 \cdot CH_3 \rightleftharpoons CH_4 + C_6H_5 \cdot CH_2$. The proposed mechanism is shown to be in conformity with hitherto observed kinetic behaviors of the reaction.

Since Hofmann and Lang¹⁾ first reported the effect of added hydrogen in promoting the rate of demethylation and in reducing the formation of polynuclear condensation products, a number of kinetic studies have been published on the thermal hydrogenolytic demethylation of methyl derivatives of benzene and naphthalene²⁾⁻⁸⁾. As have been reviewed recently⁹⁾, these works show remarkable agreements in stoichiometry as well as in reaction order for wide ranges of temperature and pressure. Thus, at temperatures ranging from 813 to 1,223°K, more than 95% of toluene conversion can be accounted for by the following stoichiometric equation: toluene + hydrogen $\longrightarrow$ benzene + methane. The reaction has been found to be first order in toluene and one-half order in hydrogen. Summarized in Table 1 are the values of kinetic parameters which have been reported by various workers. In spite of the apparent variation in reaction conditions, the values

of the rate constant are in excellent agreement at 923°K which is the average temperature at which these studies have been made. The representative values of A-factor and activation energy pertaining to the above overall stoichiometric reaction may thus be taken as $10^{11 \pm 1} l^{1/2} \cdot \text{mole}^{-1/2} \cdot \text{sec}^{-1}$ and 55 ± 5 kcal·mole⁻¹, respectively. In estimating these kinetic constants, those reported in reference 6 are weighed heavily on account of its extensiveness.

Mechanism of the reaction has not yet been discussed in any detail, except by Silsby and Sawyer²⁾ who proposed a chain reaction propagated *via* hydrogen atom which is in equilibrium with added hydrogen molecule. The latter is however based simply on a superficial analogy with *para*- to *ortho*-hydrogen conversion.

The present paper, as a continuation of a series of our communications⁵⁾⁻⁸⁾, describes a plausible mechanism of the hydrogenolysis

Table 1 Values of kinetic parameters for thermal hydrogenolysis of toluene by various workers

Ref.	Type of reactor	Temp. (°C)	Press. (atm)	A-factor ($l^{1/2} \cdot \text{mole}^{-1/2} \cdot \text{sec}^{-1}$)	Activation energy (kcal·mole ⁻¹)	Rate const. at 923°K ($l^{1/2} \cdot \text{mole}^{-1/2} \cdot \text{sec}^{-1}$)
(2)	flow	750-900	1	8.0×10^9	47	6.2×10^{-2}
(2)	flow	740-660	100	1.9	47	1.5
(5)	static	580-650	0.02	1.0	43	6.8
(7)	flow	680-740	1	9.9	50	1.6
(6)	flow	580-680	10-50	1,700	58	3.2

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in terms of a few selected elementary reactions. The selections are primarily made on the basis of the existing kinetic informations. In the absence of any reliable rate measurements, however, thermodynamic data of related compounds as well as the methods developed by Hirschfelder¹⁰⁾ and by Semenov¹¹⁾ are used to estimate kinetic parameters. This phase of investigation should be of certain significance in view of some recent commercial applications^{12),13)} and of the possible use of gaseous catalytic materials other than hydrogen in the similar process¹⁴⁾.

Thermodynamic Data of Related Substances

Listed in Table 2 are the thermodynamic data which will be used in the subsequent

Table 2 Thermodynamic data of related substances
(Standard states: ideal gas, 1 atm, 25°C)

Compounds	C_p° (cal·mole ⁻¹ ·°K ⁻¹)	S° (cal·mole ⁻¹ ·°K ⁻¹)	ΔH_f° (kcal·mole ⁻¹)
H ₂	6.9	31.2	0.0
CH ₄	8.5	44.5	-17.9
C ₆ H ₆	19.5	64.3	19.8
C ₆ H ₅ ·CH ₃	24.8	76.4	12.0
H	5.0	27.4	52.1
CH ₃	8.5	48	32.0
C ₆ H ₅	19.5	69.2	72.5
C ₆ H ₅ ·CH ₂	24.8	78	40
C ₆ H ₄ ·CH ₃	24.8	79	64

discussion. The values taken from the API Table¹⁵⁾ for stable molecules and those of hydrogen atom and methyl radical are sufficiently accurate. The values of S° for other free radicals are estimated by the authors based on symmetry and electronic degeneracy corrections to the parent hydrocarbon molecules according to the manner described by Trotman-Dickenson¹⁶⁾. The values of ΔH_f° for various free radicals are calculated from the relevant bond dissociation energies. The estimation may include errors as large as ± 2 eu in entropy and ± 2 kcal·mole⁻¹ in heat of formation. The errors would produce the uncertainty in the final evaluation of rate constant at 923°K by a factor of only three.

Initiation Reactions

The fact that the reaction takes place in

Table 3 Initiation reactions

Reactions	D_{923} (kcal·mole ⁻¹)
(1)* C ₆ H ₅ ·CH ₃ $\longrightarrow$ C ₆ H ₅ ·CH ₂ + H	81
(2) C ₆ H ₅ ·CH ₃ $\longrightarrow$ C ₆ H ₅ + CH ₃	93
(3) C ₆ H ₅ ·CH ₃ $\longrightarrow$ C ₆ H ₄ ·CH ₃ + H	105
(4) H ₂ + M $\longrightarrow$ 2·H + M	104

gaseous phase at elevated temperatures according to the rate law involving the fractional reaction order indicates a free radical chain mechanism. The elementary reactions which produce such free radicals are listed in Table 3 with the values of corresponding bond dissociation energy corrected for $923 \cdot R = 1.8$ kcal·mole⁻¹. Reactions (3) and (4) can be ignored because of the prohibitively large activation energies. Thus, the present discussion would lead to an entirely different kinetics from that of Silsby and Sawyer²⁾ who postulated reaction (4) as the initiation process. It can also be shown that the decomposition of neither benzene nor methane is important for the formation of radicals.

Selection between reactions (1) and (2) is more involved. Reaction (1) is favored on the basis of the bond dissociation energy, whereas entropy increment contributes favorably for reaction (2) which therefore becomes increasingly important at higher temperatures. If we assume that $(\Delta S_1^\ddagger - \Delta S_2^\ddagger) = (\Delta S_1 - \Delta S_2)/2 = 5.5$ eu, as seems reasonable, the ratio k_1/k_2 becomes 35 at 923°K. According to our calculation, k_2 can never exceed k_1 even for the loosest type of complex. We thus conclude that reaction (1) is the dominant source of radicals. Contrary to the statement made by Benson and Buss¹⁷⁾, who estimated that k_1 was nearly equal to k_2 at 1,100°K based on a similar calculation with slightly different thermodynamic values, we calculate that even at this temperature k_1 is still larger than k_2 by a factor of about 15.

Metathetical Reactions

Possible metathetical reactions which can be induced by either hydrogen atom or benzyl radical are listed in Table 4 with values of A-factor, activation energy and rate constant at 923°K. The method by which these kinetic parameters are assigned will now be discussed.

Table 4 Metathetical Reactions

	E (kcal·mole ⁻¹)	$\log A$ (l·mole ⁻¹ ·sec ⁻¹)	$\log k_{923}$
(5)* $C_6H_5 \cdot CH_2 + H_2 \longrightarrow C_6H_5 \cdot CH_3 + H$	28	7.7	1.10
(6) $C_6H_5 \cdot CH_2 + C_6H_5 \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_3 + C_6H_4 \cdot CH_3$	30	7.3	0.24
(7)* $C_6H_5 \cdot CH_2 + CH_4 \longrightarrow C_6H_5 \cdot CH_3 + CH_3$	30	8.7	1.64
(8) $C_6H_5 \cdot CH_2 + C_6H_6 \longrightarrow C_6H_5 \cdot CH_3 + C_6H_5$	30	7.3	0.24
(9)* $H + C_6H_5 \cdot CH_3 \longrightarrow H_2 + C_6H_5 \cdot CH_2$	4.8	9.3	8.17
(10) $H + C_6H_5 \cdot CH_3 \longrightarrow H_2 + C_6H_4 \cdot CH_3$	8.3	8.5	6.55
(11) $H + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_5$	—	—	—
(12)* $H + C_6H_5 \cdot CH_3 \longrightarrow CH_3 + C_6H_6$	—	—	—
(13) $H + CH_4 \longrightarrow H_2 + CH_3$	8.5	10	8.00
(14) $H + C_6H_6 \longrightarrow H_2 + C_6H_5$	8.3	8.6	6.65
(15)* $CH_3 + H_2 \longrightarrow CH_4 + H$	10	8.73	6.38
(16)* $CH_3 + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_5 \cdot CH_2$	8.3	8.3	6.35
(17) $CH_3 + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_4 \cdot CH_3$	10	7.5	5.15
(18) $CH_3 + C_6H_6 \longrightarrow CH_4 + C_6H_5$	10	7.6	5.25
(19) $C_6H_5 + H_2 \longrightarrow C_6H_6 + H$	6.5	7.0	5.47
(20) $C_6H_5 + C_6H_5 \cdot CH_3 \longrightarrow C_6H_6 + C_6H_5 \cdot CH_2$	5	6.6	5.43
(21) $C_6H_5 + C_6H_5 \cdot CH_3 \longrightarrow C_6H_6 + C_6H_4 \cdot CH_3$	(8)	(6)	(4)
(22) $C_6H_5 + CH_4 \longrightarrow C_6H_6 + CH_3$	7.5	7.2	5.44

The values of A_{16} and E_{16} have been determined by Trotman-Dickenson and Steacie¹⁸⁾ and are $10^{8.3}$ l·mole⁻¹·sec⁻¹ and 8.3 kcal·mole⁻¹, respectively. The values of kinetic parameters for reaction (7) which is the reverse of the former are therefore $10^{8.7}$ l·mole⁻¹·sec⁻¹ and 30 kcal·mole⁻¹, respectively. Also estimated from A_{16} is the value of A_9 . Based on the empirical regularity observed in the series of similar reactions assembled in Table 5¹⁹⁾, A-

Table 5 A-factors for hydrogen atom abstraction by hydrogen and methyl radical

Reactions	$\log A$
$H + C_2H_5 \longrightarrow H_2 + C_2H_5$	9.49
$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	8.47
$H + C_3H_8 \longrightarrow H_2 + C_3H_8$	8.98
$CH_3 + C_3H_8 \longrightarrow CH_4 + C_3H_7$	7.96
$CH_3 + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_5 \cdot CH_2$	8.31

factors for hydrogen atom abstraction from a given hydrocarbon molecule are larger with hydrogen atom than with methyl radical by a nearly constant factor of about 10. Thus, a figure $10^{9.3}$ l·mole⁻¹·sec⁻¹ is expected for A_9 at 923°K. For the value of E_9 , both Hirschfelder's and Semenov's empirical rules would predict about 4.8 kcal·mole⁻¹. The kinetic parameters for reaction (5), which is the reverse of reaction (9), would then become $10^{7.7}$ l·mole⁻¹·sec⁻¹ and 28 kcal·mole⁻¹

based on the changes in entropy and enthalpy associated with the reversible system.

Exactly the same method as described for reaction (9) can also be applied for reaction (20). Thus the values of A_{20} and E_{20} are estimated to be $10^{6.6}$ l·mole⁻¹·sec⁻¹ and 5 kcal·mole⁻¹, respectively. Table 6 includes

Table 6 A-factors for hydrogen atom abstraction by various radicals

Reactions	$\log A$
$H + H_2 \longrightarrow H_2 + H$	10.4
$CH_3 + H_2 \longrightarrow CH_4 + H$	8.73
$C_6H_5 + H_2 \longrightarrow C_6H_6 + H$	7.01
$H + CH_4 \longrightarrow H_2 + CH_3$	10.0
$C_6H_5 + CH_4 \longrightarrow C_6H_6 + CH_3$	7.23
$H + C_6H_5 \cdot CH_3 \longrightarrow H_2 + C_6H_5 \cdot CH_2$	9.33
$CH_3 + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_5 \cdot CH_2$	8.31

the values of A-factor observed for a series of similar reactions which are used for the extrapolation¹⁹⁾. The kinetic parameters for reaction (8) are, consequently, $10^{7.3}$ l·mole⁻¹·sec⁻¹ and 30 kcal·mole⁻¹. These latter values are also assumed for reaction (6) because of the structural similarity between reactions (6) and (8).

The following kinetic constants have been obtained by Fielding and Prichard²⁰⁾ and by Trotman-Dickenson and Steacie¹⁸⁾: $E_{18}=10.3$ kcal·mole⁻¹, $E_{19}=6.5$ kcal·mole⁻¹, $E_{22}=7.5$

kcal·mole⁻¹, $A_{18}=10^{7.6}$ l·mole⁻¹·sec⁻¹, $A_{19}=10^{7.0}$ l·mole⁻¹·sec⁻¹, and $A_{22}=10^{7.2}$ l·mole⁻¹·sec⁻¹. The values of A_{14} and E_{14} now become $10^{8.8}$ l·mole⁻¹·sec⁻¹ and 8.3 kcal·mole⁻¹, respectively, in relation with A_{19} and E_{19} . These values are also assumed for reaction (10) with a slight modification on the A-factor. A similar relation holds between reactions (17) and (18), and the values of A_{17} and E_{17} are $10^{7.5}$ l·mole⁻¹·sec⁻¹ and 10 kcal·mole⁻¹, respectively.

The value of E_{21} is estimated to be at least 8 kcal·mole⁻¹ which is approximately the minimum energy required to abstract hydrogen atom from aromatic nucleus. Also deduced is the value of $A_{21}=10^{6.0}$ l·mole⁻¹·sec⁻¹ from the series of similar reactions listed in Table 7.

Table 7 A-factors for hydrogen atom abstraction by various radicals

Reactions	log A
$H + H_2 \longrightarrow H_2 + H$	10.4
$H + C_6H_5 \cdot CH_3 \longrightarrow H_2 + C_6H_4 \cdot CH_3$	8.50
$CH_3 + H_2 \longrightarrow CH_4 + H$	8.73
$CH_3 + C_6H_5 \cdot CH_3 \longrightarrow CH_4 + C_6H_4 \cdot CH_3$	7.50
$C_6H_5 + H_2 \longrightarrow C_6H_6 + H$	7.01

The values assigned for reaction (15) ($E_{15}=10$ kcal·mole⁻¹ and $A_{15}=10^{8.7}$ l·mole⁻¹·sec⁻¹) are those observed by Whittle and Steacie²¹⁾. Thus the values of A_{13} and E_{13} would become $10^{10.0}$ l·mole⁻¹·sec⁻¹ and 8.5 kcal·mole⁻¹, respectively.

Since the overall hydrogenolysis requires the splitting of methyl group from aromatic nucleus, at least either reaction (11) or reaction (12) must be involved in the reaction. Any reliable estimation of the kinetic parameters for such *atomic cracking* process would be impossible at present. In the present paper, reaction (12) is selected in view of a larger enthalpy decrease associated with this reaction. This latter reaction has also been suggested in a number of other papers²²⁾.

The values of rate constants at 923°K evaluated for all metathetical reactions considered above are listed in the last column of Table 4. The comparison of these values and the relative concentration of the reactant species would permit the selection of more

important reactions which are marked by asterisk in the table.

Termination Reactions

The mode of termination reaction is mainly determined by the relative concentration of radicals present in the reaction system, since the activation energy for radical recombinations can be considered to be nearly zero. Since reactions (5) and (12) have been shown to be the slower processes, the following sequence can be expected for the steady-state concentration of the radicals: $(C_6H_5 \cdot CH_2)_{ss} \gg (H)_{ss} > (CH_3)_{ss} \gg (C_6H_5)_{ss}$. Thus the reactions which may possibly participate in radical consumption would be those listed in Table 8.

Table 8 Termination reactions

(23) $C_6H_5 \cdot CH_2 + C_6H_5 \cdot CH_2 \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$
(24) $C_6H_5 \cdot CH_2 + C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$ $\longrightarrow C_6H_5 \cdot CH_3 + C_6H_5 \cdot CH \cdot CH_2 \cdot C_6H_5$
(25)* $C_6H_5 \cdot CH_2 + H \longrightarrow C_6H_5 \cdot CH_3$

Recombination of two benzyl radicals to form bibenzyl, reaction (23), can not serve as an effective termination process by itself, because of the extremely weak central C-C linkage of the resulting molecule. Therefore in order that reaction (23) competes with reaction (25), bibenzyl should be consumed through reaction (24) with faster rate than reaction (25). This would not be the case at a relatively high hydrogen atom concentration as in the present study. It should be noted that the discussion above is a consequence of the considerable diminution of benzyl radical through reaction (5).

Mechanism of Toluene Hydrogenolysis

Based on the discussion given above, the mechanism of the hydrogenolysis of toluene can best be represented by the following set of elementary reactions.

This scheme is a chain reaction with the overall stoichiometry corresponding to the observed hydrogenolysis. Reactions (a) and (b) serve as the initiation and the termination; while reactions (e) and (f) the propagation *via* hydrogen atom, and reactions (c), (d), (g) and (h) the radical transfer. The effect of the initially added hydrogen is characterized by the presence of reactions (d) and (f) both of which should be an extremely minor contribution in the case of the *straight pyrolysis*. These latter reactions prevent the accumulation of benzyl radical resulting in less formation of higher boiling materials. The proposed mechanism indicates that the presence of any foreign material which increases hydrogen atom concentration would also promote the rate of the *atomic cracking*.

At steady-state the stationary concentration of radicals can be expressed by the following equations:

$$\begin{aligned} (\text{C}_6\text{H}_5 \cdot \text{CH}_2)_{ss} &= \left(\frac{k_a \cdot k_c}{k_b \cdot k_d} \right)^{1/2} \frac{(\text{C}_6\text{H}_5 \cdot \text{CH}_3)}{(\text{H}_2)^{1/2}}, \\ (\text{H})_{ss} &= \left(\frac{k_a \cdot k_d}{k_b \cdot k_c} \right)^{1/2} (\text{H}_2)^{1/2}, \\ (\text{CH}_3)_{ss} &= \frac{k_e}{k_f} \cdot \left(\frac{k_a \cdot k_d}{k_b \cdot k_c} \right)^{1/2} \frac{(\text{C}_6\text{H}_5 \cdot \text{CH}_3)}{(\text{H}_2)^{1/2}} \\ &\quad + \frac{k_h}{k_f} \left(\frac{k_a \cdot k_c}{k_b \cdot k_d} \right)^{1/2} \frac{(\text{C}_6\text{H}_5 \cdot \text{CH}_3)(\text{CH}_4)}{(\text{H}_2)^{3/2}}. \end{aligned}$$

These approximate expressions are accurate to within 3% at the average experimental conditions. In agreement with the experimentally observed rate equation, the overall rate equation is thus:

$$-d(\text{C}_6\text{H}_5 \cdot \text{CH}_3)/dt = k_e \cdot (k_a \cdot k_d / k_b \cdot k_c)^{1/2} \cdot (\text{C}_6\text{H}_5 \cdot \text{CH}_3) \cdot (\text{H}_2)^{1/2}.$$

Therefore the overall values of A-factor and activation energy can be expressed in terms of individual kinetic parameters by the following equations:

$$\begin{aligned} A_{\text{overall}} &= A_e \cdot (A_a \cdot A_d / A_b \cdot A_c)^{1/2} \\ &= A_e \cdot 10^{3.06} \text{ l}^{1/2} \cdot \text{mole}^{-1/2} \cdot \text{sec}^{-1}, \\ E_{\text{overall}} &= E_e + 1/2(E_a - E_b - E_c + E_d) \end{aligned}$$

$$= E_e + 51.6 \text{ kcal} \cdot \text{mole}^{-1}.$$

The experimentally obtained kinetic parameters would thus place the values of A_e and E_e to be approximately $10^8 \text{ l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ and $5 \text{ kcal} \cdot \text{mole}^{-1}$, respectively. Both of these values can be considered reasonable. The gratifying agreements in the kinetic features are taken for the support of the proposed mechanism.

References

- Hofmann, F., Lang, K., *Brennst. Chem.*, **10**, 203 (1929).
- Silsby, R. I., Sawyer, E. W., *J. Appl. Chem.*, **6**, 347 (1956).
- Betts, W. D., Pepper, F., Silsby, R. I., *J. Appl. Chem.*, **7**, 497 (1957).
- Betts, W. D., Pepper, F., *J. Appl. Chem.*, **8**, 509 (1958).
- Matsui, H., Amano, A., Tokuhisa, H., *Bull. Petrol. Inst. (Japan)*, **1**, 67 (1959).
- Tsuchiya, A., Hashimoto, A., Tominaga, H., Masamune, Sh., *Bull. Petrol. Inst. (Japan)*, **1**, 73 (1959).
- Masamune, Sh., Amano, A., Tokuhisa, H., *Tech. Reports Tohoku Univ. (Japan)*, **25**, (1), 27 (1960).
- Masamune, Sh., Uchiyama, M., Tokuhisa, H., *Tech. Reports Tohoku Univ. (Japan)*, **25**, (1), 39 (1960).
- Weiss, A. H., *Petrol. Refiner*, **41**, (6), 185 (1962).
- Hirschfelder, J., *J. Chem. Phys.*, **9**, 645 (1941).
- Semenov, N. N., "Some Problems in Chemical Kinetics and Reactivity," (English translation), Vol. I, 29 (1958). Princeton Univ. Press, Princeton.
- Oil Gas J.*, **59** (March 6), 80 (1961).
- Stormont, O. H., *Oil Gas J.*, **60** (Nov. 13), 160 (1961).
- Tokuhisa, H., Tanji, H., Patent in application.
- Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimental, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," (1953). Carnegie Press, Pittsburgh.
- Trotman-Dickenson, A. F., *J. Chem. Phys.*, **21**, 211 (1953).
- Benson, S. W., Buss, J. H., *J. Phys. Chem.*, **61**, 104 (1957).
- Trotman-Dickenson, A. F., Steacie, E. W. R., *J. Chem. Phys.*, **19**, 329 (1951).
- Benson, S. W., "The Foundations of Chemical Kinetics," Tables XII 5 and 6 (1960). McGraw-Hill Co., New York.
- Fielding, W., Prichard, H. O., *J. Phys. Chem.*, **66**, 821 (1962).
- Whittle, E., Steacie, E. W. R., *J. Chem. Phys.*, **21**, 993 (1953).
- de Darwent, B., *Discussion Faraday Soc.*, No. 14, 129 (1953).