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Mechanism of Hydrogenolysis. II. A Molecular Orbitals Study of Hydrogenolysis of Toluene

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In hydrogenolysis of toluene to produce benzene and methane, atomic cracking process $H+C_6H_5CH_3 \rightarrow C_6H_6CH_3$ (*a*) or $H+C_6H_5CH_3 \rightarrow C_6H_5+CH_4$ (*b*) has been presumed as rate controlling in chain propagation step of the radical chain mechanism. These two alternative processes are compared on the energetics calculated by the extended Hückel M.O. method. The reaction (*a*), an addition of the attacking hydrogen atom to phenyl carbon atom adjacent to methyl group followed by an elimination of methyl radical in a concerted manner, is found to be the most likely pathway.

In the last decade a considerable number of kinetic investigations have been reported on the thermal hydrogenolytic demethylation of toluene.[1] The reaction can be expressed by the stoichiometry,

$$C_6H_5CH_3 + H_2 \longrightarrow C_6H_6 + CH_4,$$

and is sufficiently clean for rate measurements. The observed rates can be described within the specified deviations by

$$-d[C_6H_5CH_3]/dt = k[C_6H_5CH_3][H_2]^{1/2} \text{ mol}\cdot l^{-1}\cdot\text{sec}^{-1},$$
$$k = 10^{(11\pm1)-(55\pm5)/\theta},$$

where θ being $(2.303\,\boldsymbol{R}T)$ in kcal mol^{-1}.

The values of Arrhenius kinetic parameters and the overall three-halves order were interpreted by these authors in terms of a free radical chain mechanism, which was subsequently supported by Benson and Shaw.[2b] The chain propagation step was controlled by the following *atomic cracking* process:[2a]

$$H + C_6H_5CH_3 \xrightarrow{(a)} C_6H_6 + CH_3, \text{ or}$$
$$H + C_6H_5CH_3 \xrightarrow{(b)} C_6H_5 + CH_4$$

The latter alternative was suggested by Silsby and Sawyer,[1a] and also by Burr, Meyer and Strong.[1c] However, exact mechanistic natures of the reactions have not hitherto been discussed in any detail. In the present paper a comparison will be made on the energetics between the two reactions; perpendicular approach of hydrogen atom to phenyl carbon atom to which methyl group is attached (reaction (*a*)) on one hand, and direct Walden inversion type hydrogen attack to methyl carbon atom (reaction (*b*)) on the other. The comparison is to be based on the total electron energy calculations of the postulated transition structures using the extended Hückel M.O. method. As will be discussed in the present paper, reaction (*a*) is the most likely pathway in hydrogenolytic demethylation. The *atomic cracking* is, therefore, an addition of hydrogen atom to phenyl carbon followed by an elimination of methyl radical in a concerted manner.

Molecular Orbitals Calculation

To investigate which one of the two alternative reaction mechanisms is operative, the changes in total electron energies of the transition structures along presumed reaction coordinates are calculated. An empirical molecular orbitals theory developed by Hoffmann,[3] that is, extended Hückel method is employed which has proved useful in discussing the hydrocarbon conformational problems such as barriers to internal rotation, geometric iso-

1) a) R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956); W. D. Betts, F. Popper and R. I. Silsby, *ibid.*, **7**, 497 (1957). b) H. Matsui, A. Amano and H. Tokuhisa, *Bull. Japan Petrol. Inst.*, **1**, 67 (1959); A. Tsuchiya, A. Hashimoto, H. Tominaga and S. Masamune, *ibid.*, **1**, 73 (1959); S. Masamune, A. Amano and H. Tokuhisa, *Tech. Reports Tohoku Univ.* (Japan), **25**(**1**), 27 (1960); H. Morii, A. Hashimoto and H. Tominaga, World Petrol. Congr. 6th, Frankfurt, Germany (1963). c) J. G. Burr, R. A. Meyer and J. D. Strong, *J. Amer. Chem. Soc.*, **86**, 3846 (1964).

2) a) A. Amano, H. Tominaga and H. Tokuhisa, *Bull. Japan Petrol. Inst.*, **7**, 59 (1965). b) S. W. Benson and R. Shaw, *J. Chem. Phys.*, **47**, 4052 (1967).

merism,[3] as well as electronic structure of transient species.[4]

The secular determinant, with the order of $(4n+m)$ for a molecule C_nH_m, of which atomic orbitals are $2s$, $2p_x$, $2p_y$, $2p_z$ for carbon and $1s$ for hydrogen, is solved using an electronic computor HITAC 5020 for eigen values ε_i and eigen vectors C_{pi} of the molecular orbitals. The complete secular determinant is treated, namely, all overlap integrals computed, and off diagonal E's retained. The Coulomb integrals H_{pp} are chosen as valence state ionization potentials of Pritchard and Skinner.[5] The reasonance integrals H_{pq} are approximated as

$$H_{pq} = 0.5K(H_{pp}+H_{qq})S_{pq},$$

where

$$K = 1.75,$$

after the original proposal by Hoffmann.[3] The effective nuclear charges of Slater orbitals are employed.[6] The ovelap integrals S_{pq} are calculated by Mulliken's procedure.[7] For radicals and transient species with odd number of electrons, the highest orbital is assumed to be half-occupied.

Reaction Co-ordinate and Conformation

The configuration of toluene molecule is presented in Fig. 1, where large open circles indicate carbon atom and small full circles hydrogen atom. The bond lengths and angles are found in chemical dictionary.

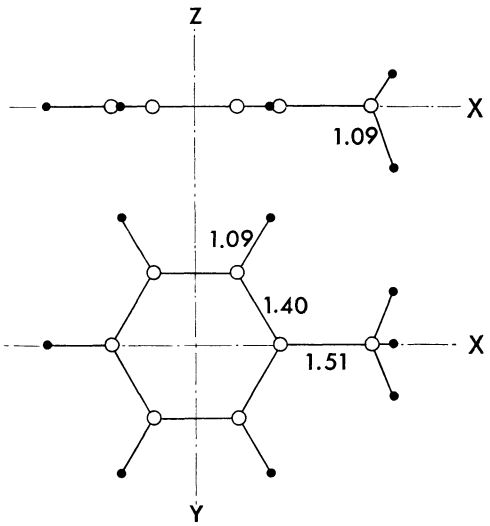
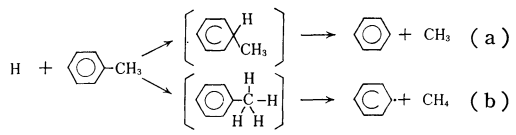


Fig. 1. Conformation of toluene.

Reactions (*a*) and (*b*) are considered to proceed through the following transition states, respectively;



The former route denotes the approach of hydrogen atom to the phenyl carbon atom adjacent to methyl group in perpendicular direction to toluene ring plane. This forms the σ-complex with pseudo sp^3 hybrid structure, ending with the elimination of methyl radical to form benzene. While the latter signifies the approach of hydrogen atom to the methyl carbon atom in the horizontal direction along methyl - ring (C7-C1) axis. Through penta - valent carbon complex, this results in Walden type inversion to form phenyl radical and methane.

Perspective sketched for the two transient species are illustrated in Figs. 2 and 3, where H16 stands

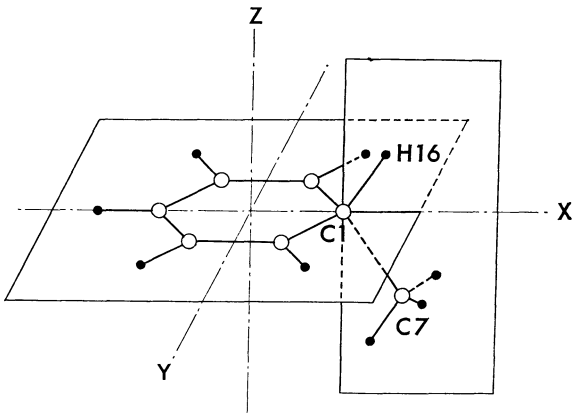


Fig. 2. Perspective view of transition state for reaction (a).

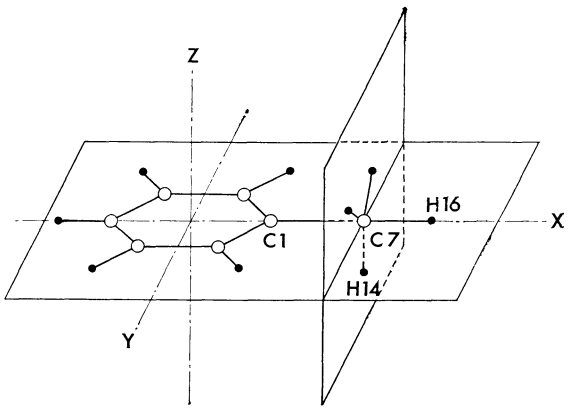


Fig. 3. Perspective view of transition state for reaction (b).

3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
4) H. Kato, K. Morokuma, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1749 (1965).
5) H. O. Pritchard and H. A. Skinner, *Trans. Faraday Soc.*, **49**, 1254 (1953).
6) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).
7) R. S. Mulliken, C. A. Ricke and D. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

Table 1. Change of total electron energy with approach of attacking hydrogen atom along vertical (z) axis

No.	Bond length, Å		Bond angle		Conformation	Total electron energy, eV.	Energy level of half-filled orbital, eV
	Cl-H16	C1-C7	∠H16-C1-x	∠C7-C1-x			
I[a]	5.0	1.51	90°	0°	Toluene	−645.79	—
II	3.0	1.51	90°	0°	Toluene	−645.75	—
III	2.0	1.52	80°	25°	Toluene	−645.53	—
IV	1.5	1.53	70°	35°	Toluene	−645.67	−10.750
V	1.5	1.53	70°	35°	Cyclohexadienyl	−646.04	−10.432
	1.22	1.53	60°	60°	Cyclohexadienyl	−646.81	—
	1.22	1.68	60°	60°	Cyclohexadienyl	−647.50	—
VI[b]	1.11	1.54	55°	55°	Cyclohexadienyl	−647.21	−10.439
	1.11	1.68	60°	60°	Cyclohexadienyl	−647.62	—
VII[c]	1.10	2.00	25°	80°	Benzene and methyl	−647.24	—
VIII	1.09	3.0	0°	90°	Benzene and methyl	−649.28	—
IX	1.09	5.0	0°	90°	Benzene and methyl	−649.42	—

Remarks
a) Refer to Fig. 1 for the conformation of toluene.
b) Refer to Fig. 4. The conformation of cyclohexadienyl is proposed by Russel S. Drago and Harold Peterson, Jr.
c) CH_3 in the ground state, $2A_2''$, is taken as planar with a CH distance of 1.08 Å after G. Herzberg.

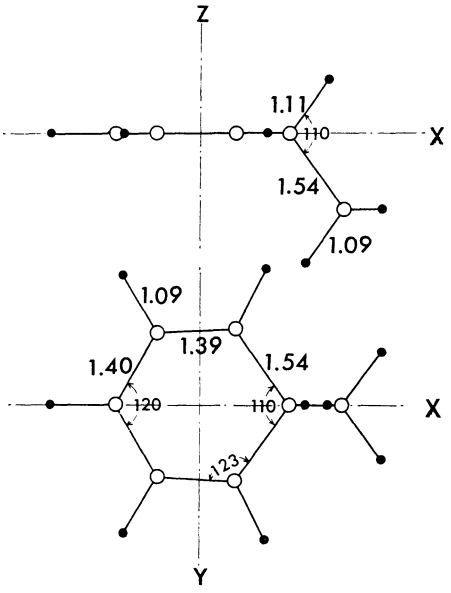
Table 2. Change of total electron energy with approach of attacking hydrogen atom along horizontal C1-C7 (x) axis

No.	Bond length, Å		Bond angle	Confromation		Total electron energy, eV
	C7-H16	C1-C7	∠H14-C7-C1	Phenyl	Methyl	
I′	5.0	1.51	109°28′	Toluene		−645.79
II′	3.0	1.51	109°28′	Toluene		−645.71
III′	2.0	1.51	100°	Toluene		−644.32
IV′	1.5	1.60	95°	Benzene	Shallow pyramid	−643.18
V′	1.3	1.66	90°	Benzene	Planar	−643.55
	1.3	1.81	90°	Benzene	Planar	−644.11
	1.3	1.90	90°	Benzene	Planar	−644.33
VI′	1.2	1.81	90°	Benzene	Planar	−644.19
	1.3	1.66	90°	Benzene	Planar	−643.66
VII′	1.15	2.0	85°	Benzene	Shallow pyramid	−644.71
VIII′[a]	1.09	3.0	70°32′	Benzene	Methane	−648.23
IX′[b]	1.09	5.0	70°32′	Benzene	Methane	−648.44

Remarks
a) Conformation of phenyl radical is taken as the same with that of benzene except one ring hydrogen lost. Refer to G. Porter and B. Ward.
b) Conformation of methane; CH bond length 1.09 Å with bond angle ∠HCH 109°28′.

for the attacking hydrogen atom, Cl the phenyl carbon atom adjacent to the methyl group, and C7 the carbon atom of the methyl group to be removed. The total electron energies of 24 transient species are calculated based on the conformational parameters listed in Tables 1 and 2. The distance between Cl and H16, or C7 and H16, is arbitrarily chosen as reaction co-ordinate. The calculation covers the range from 5 Å to 1.09 Å that is equivalent to the normal C–H bond length for benzene or methane. With the approach of H16, the bond length Cl-C7 correspondingly increases from the original 1.51 Å to 5 Å and the bond angles also change as are shown in the tables. In this course the C–H bond length of methyl group is assumed to remain constant at 1.09 Å with a sole exception of 1.08 Å for methyl radical.

The conformation of σ-complex, VI in Table 1, is presumed as is shown in Fig. 4 based on that of cyclohexadienyl radical proposed by Drago and



METHYL CYCLOHEXADIENYL RADICAL

Fig. 4. Conformation of methyl cyclohexadienyl radical.

Peterson.[8] As for the penta-valent carbon complexes, V′ and VI′ in Table 2, the bond distance C7-H16 (or C1-C7) is taken as 20% (or 10%) longer than that of methane (or of toluene) for V′, and *vice versa* for VI′. The conformation of methyl radical is taken as planar with C–H distances of 1.08 Å as is presented by Herzberg.[9] Phenyl radical is supposed to have the same conformation with that of benzene except that one hydrogen atom is lost. This is suggested by Porter and Ward.[10]

At a given reaction co-ordinate, namely at a given approach of the attacking hydrogen atom to carbon atom C1 or C7, effects of some changes in C1-C7 bond distance or bond angle are evaluated. Indicated are the lower total electron energies for the transient species with the longer bond distances between departing carbon atoms. The formation of these transient species with the lower energies, however, seems less favoured due to the less chance of hydrogen atom attack on one of the carbon atoms with the C1-C7 bond which is longer than in equilibrium and in vibration.

Results and Discussion

Indicated in Fig. 5 are the changes in total electron energies of the reacting systems with the two different ways of approach of attacking hydrogen

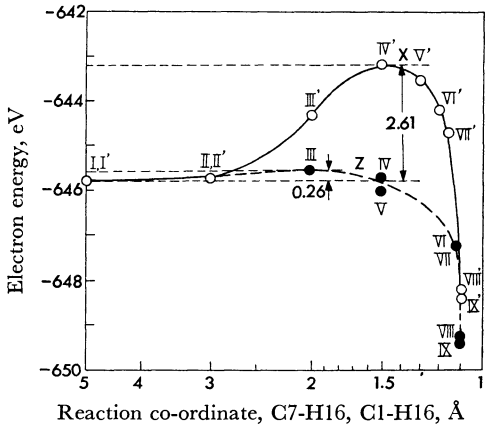


Fig. 5. Reaction co-ordinate energy diagram for reactions (a) and (b).

atom. It is clearly demonstrated that the approach to C1, the phenyl carbon atom, in parallel with z axis requires much less energy than the approach to C7, the methyl carbon atom, along x axis does. The energy barrier of the former reaction route, E_z, is calculated as 0.26 eV (*ca.* 6 kcal mol^{-1}) while that of the latter, E_x, is approximated as 2.61 eV (*ca.* 60 kcal mol^{-1}), 10 times larger than E_z. The value E_x=60 kcal mol^{-1} does not seem exceedingly large in view of the high activation energies that are generally associated with ionic Walden inversion reactions.

The value E_z=6 kcal mol^{-1}, on the other hand, is in surprisingly good agreement with the value of 5 kcal mol^{-1} predicted by these authors.[2a] They have evaluated the kinetic parameters of a number of possible elementary reactions involved in the thermal hydrogenolysis of toluene based on the bulk of kinetic and thermodynamic informations. More important elementary reactions are thus selected, and the following formulation is obtained to describe the main scheme of the hydrogenolysis:

$$C_6H_5CH_3 \underset{2}{\overset{1}{\rightleftharpoons}} C_6H_5CH_2 + H$$

$$H + C_6H_5CH_3 \underset{4}{\overset{3}{\rightleftharpoons}} H_2 + C_6H_5CH_2$$

$$H + C_6H_5CH_3 \xrightarrow{(a)} C_6H_6 + CH_3$$

$$CH_3 + H_2 \underset{6}{\overset{5}{\rightleftharpoons}} CH_4 + H$$

$$CH_3 + C_6H_5CH_3 \underset{8}{\overset{7}{\rightleftharpoons}} CH_4 + C_6H_5CH_2$$

The proposed mechanism is shown to be in conformity with hitherto observed kinetic behaviours of the reaction. Assuming steady-state approximation, the overall rate equation is given by the equation:

$$-d[C_6H_5CH_3]/dt \fallingdotseq k_a\left(\frac{k_1 \cdot k_4}{k_2 \cdot k_3}\right)^{1/2}[C_6H_5CH_3][H_2]^{1/2}$$

8) R. S. Drago and H. Peterson, Jr., *J. Amer. Chem. Soc.*, **89**, 3978 (1967).
9) G. Herzberg, *Proc. Roy. Soc.*, **262A**, 291 (1961).
10) G. Porter and B. Ward, *Proc. Chem. Soc.*, **1964**, 288.

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

$$A \text{ overall} = A_a(A_1A_4/A_2A_3)^{1/2}$$
$$= A_a \cdot 10^{3.06}\ l^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{sec}^{-1}$$
$$E \text{ overall} = E_a + \frac{1}{2}(E_1 - E_2 - E_3 + E_4)$$
$$= E_a + 51.6\ \text{kcal} \cdot \text{mol}^{-1}$$

The comparison of these theoretical values with the experimental ones would thus place the values of A_a and E_a as approximately 10^8 l mol^{-1} sec^{-1} and 5 kcal mol^{-1}, respectively. The value E_a coincides fairly well with the value E_z obtained in the present paper.

The calculated values of E_z=6 kcal mol^{-1} is also supported by some experiments. In the gamma radiolysis of propane, Kan Yang[11] observed the rate of formation of hydrogen is reduced by the presence of olefins or benzene. The effect of temperature on this inhibition indicates that it results from the hydrogen atom addition to olefins or benzene. The activation energy of 3.5 kcal mol^{-1} is obtained for benzene and can be compared to the value E_z=6 kcal mol^{-1}. Myran C. Sauer, Jr. and Barry Ward used the technique of pulsed radiolysis obtaining the rate constants at 25°C for the gas phase reaction of hydrogen atoms with benzene and toluene as 0.37×10^8 and 1.0×10^8 l mol^{-1} sec^{-1}, respectively.[12] The activation energy in the case of benzene is about 3 kcal mol^{-1}. Benzene and toluene was found to yield the cyclohexadienyl and methylcyclohexadienyl radicals, respectively, with absorption maxima at 302 and 307 mμ, respectively, in the gas phase. These experimental data are also in excellent agreement with the calculated kinetic parameters aforementioned.

This agreement might be rather fortuitous, because neither nuclear nor electronic repulsion is explicitly considered in the extended Hückel molecular orbitals calculation. Development of a more advanced molecular orbitals treatment and its application to this study is now in progress in this laboratory.

Conclusion

These considerations lead to the conclusion that the atomic cracking of toluene by hydrogen atom is a radical substitution proceeding through a methylcyclohexadienyl radical type σ-complex, to give benzene and methyl radical in a concerted manner. The validity of this conclusion may be further supported by the previous study[13] where the effect of methyl substitution on the hydrogenolytic demethylation of polymethylbenzenes has been discussed in terms of reactivity index deduced from molecular orbitals theory.

11) Kan Yang, *J. Amer. Chem. Soc.*, **84**, 3795 (1962).

12) Myran C. Sauer, Jr., and Barry Ward, *J. Phys. Chem.*, **71**, 3971 (1967).

13) A. Amano, M. Uchiyama, Y. Sato, H. Tominaga, H. Arai and T. Kunugi, This Bulletin, **43**, 3653 (1970).