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Mechanism of Hydrogenolysis. III. Thermal Hydrogen Exchange and Demethylation of Toluene-2-d_1, -3-d_1, and -4-d_1

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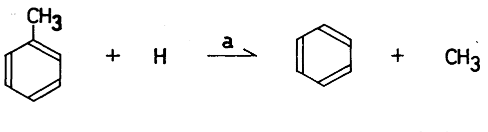
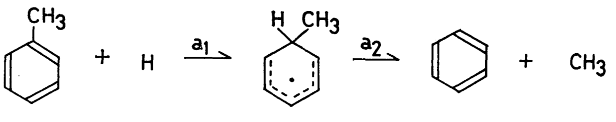
Rates of gas phase thermal hydrogen exchange and hydrogenolytic demethylation of toluene-2-d_1, -3-d_1, and -4-d_1 are evaluated using flow apparatus at temperatures 675—750 °C in the presence of a large excess molecular hydrogen. Both the exchange and the demethylation obey three-halves order rate law indicating the chain mechanism carried by hydrogen atom, the former being found slightly faster than the latter. Rate parameters of the two reactions taking place concurrently are then correlated with the extended Hückel superdelocalizability values appropriate to methylcyclohexadienyl transient formation. Overall applicability of the dynamic index as a measure of reactivity of deuteriotoluenes toward hydrogen atom attack is taken as an additional support for the generally accepted chain mechanism whose rate-determining step consists of electroneutral hydrogen atom addition to aromatic nucleus.

Gas phase demethylation of a series of methyl substituted benzenes in a stream of a large excess hydrogen has been a subject of numerous investigations.[1] General features of the reaction including product distribution and kinetic behavior can be accounted for by the free radical chain mechanism in which the following atomic cracking process (*reaction a*) assumes the rate-controlling role.[2]



The process may be looked upon as consisting of the addition of attacking hydrogen atom to the phenyl carbon adjacent to methyl group followed by the elimination of methyl radical through the intermediary formation of methylcyclohexadienyl radical.



It has been shown that the rate of the consecutive sequence described above is determined by addition (*reaction* a_1).[3] Attempts had hitherto been made to correlate either the atom localization energy[4] or the maximum free valence[5] with observed free radical addition rate constants, showing that these *static reactivity indices* were in limited practical use. However, the ease with which the key reaction proceeds could be predicted by the modified superdelocalizability values, the *dynamic reactivity index* S_r(R) proposed by Fukui

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[1] a) H. Matsui, A. Amano, and H. Tokuhisa, *Bull. Jap. Petrol. Inst.*, **1**, 67 (1959); S. Masamune, A. Amano, and H. Tokuhisa, *Tech. Reports Tohoku Univ.* (Japan), **25**,(1) 27 (1960); S. Masamune, M. Uchiyama, and H. Tokuhisa, *ibid.*, **25**(1), 39 (1960). b) A. Amano, M. Uchiyama, Y. Sato, H. Tominaga, H. Arai, and T. Kunugi, This Bulletin, **43**, 3653 (1970).

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

[3] H. Tominaga, H. Arai, T. Kunugi, A. Amano, M. Uchiyama, and Y. Sato, This Bulletin, **43**, 3658 (1970).

[4] F. H. Burkitt, C. A. Coulson, and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[5] B. Pullman, *J. Chim. Phys.*, **55**, 790 (1958).

et al.[6] of the ring carbon atom at which the addition-elimination takes place.[1]

The extended Hückel calculation on toluene, however, gives the values of S_r(R) which indicate that phenyl hydrogen is more susceptible to substitution than methyl group upon hydrogen atom attack. A qualitative evidence for this has been provided by Burr *et al.* in their study on the pyrolysis of deuterium laveled toluene.[7] Isotopic distribution in the product observed can only be explained on the assumption that hydrogen-deuterium exchange is slightly faster than demethylation.

In the present work, rate of hydrogen-deuterium exchange relative to that of demethylation has been evaluated using toluene-2-d$_1$, -3-d$_1$, and -4-d$_1$ as reactants. Results are then correlated with the relevant S_r(R) values. In so doing, we expect to extend the applicability of the concept of the superdelocalizability to radical substitutions and also to provide an additional support for the mechanism of hydrogenolysis. Some characteristic features of the key reaction are envisaged during the course of the present approach and will also be reported.

Experimental

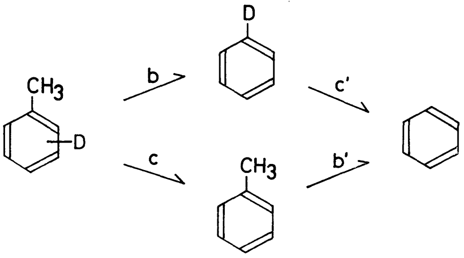
Toluene-2-d$_1$, -3-d$_1$ and -4-d$_1$ were prepared by the methods of Fukuda *et al.*[8] and Weldon *et al.*[9] with minor modifications from *o*-chloro, *m*-bromo and *p*-bromo derivatives of toluene, respectively. Gas chromatographic analysis revealed that the synthetic materials purified through conventional distillation consisted of more than 99.8 mol% toluene fraction accompanied by a trace amount of ether. Infrared absorption spectra were in good agreement with those of toluene-d$_1$'s reported by Turkevich *et al.*[10] and by Tiers.[11] The synthetic materials were passed through a reaction vessel and the fraction collected as unreacted toluene was used in the subsequent rate measurements. Cylinder hydrogen, 99.9 mol% purity as analyzed by mass-spectrometry, was used after conventional purification.

Rates of the reaction of each toluene-d$_1$ were measured by a flow apparatus specially designed for sufficient accuracy in both temperature and residence time. Details of the apparatus and procedures were described elsewhere.[12]

Liquid products were introduced into a gas chromatographic apparatus with a 3 *m*-Apiezon Grease L packed column for analysis of total isotopic benzenes. A Perkin-Elmer 337 Infrared Spectrometer, equipped with KBr optics and effective slit width of approximately 25 microns, was then used to analyze toluene fraction for deuterium distribution at wave lengths 21.62, 21.93, 22.10 and 22.12 mμ for toluene, toluene-2-d$_1$, toluene-3-d$_1$ and toluene-4-d$_1$, respectively.

Results and Discussion

Stoichiometry. Liquid products from each of the three isomeric toluene-d$_1$'s mainly consisted of benzene, benzene-d$_1$ and toluene together with unreacted toluene-d$_1$. No intramolecular migration of deuterium in toluene-d$_1$ was detected. Hydrocarbons of higher molecular weight were also present, but they did not amount to more than a few percent of toluene-d$_1$ reacted. The gas phase thermal reaction of toluene-d$_1$ thus consists of simultaneous hydrogenolytic demethylation (*reactions b* and *b'*) and hydrogen-deuterium exchange (*reactions c* and *c'*).



Kinetics. The results of the rate measurements for both demethylation and exchange of toluene-2-d$_1$, toluene-3-d$_1$, and toluene-4-d$_1$ are listed in Tables 1, 2, and 3, respectively. They exhibit validity of the overall

Table 1. Rates of demethylation and exchange of toluene-2-d$_1$

Temp. (°C)	H$_2$/reactant (mol/mol)	Residence time (s)	Conversion (mol %)		Three-halves order rate constant[a)] (l$^{1/2}$ mol$^{-1/2}$ s^{-1})	
			demethylation	exchange	demethylation	exchange
675.0	5.00	8.33	3.68	10.00	0.0458	0.0827
	4.97	4.20	2.00	9.97		
700.0	5.05	10.90	10.40	16.00	0.1039	0.1510
	5.03	8.18	7.91	10.73		
	5.06	5.44	5.33	8.78		
	5.08	4.08	4.13	6.56		
	5.34	1.96	1.97	2.44		
725.3	5.10	3.97	7.38	9.86	0.1983	0.2560
750.2	5.17	1.93	6.90	8.27	0.3836	0.4877
	5.04	1.32	4.90	7.56		

a) Evaluated by the least-squares method for three-halves order plots of the relevant data.

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6) H. Kato, K. Morokuma, T. Yonezawa, and K. Fukui, This Bulletin, **38**, 1749 (1965).

7) J. G. Burr, R. A. Meyer, and J. D. Strong, *J. Amer. Chem. Soc.*, **86**, 3846 (1964).

8) T. Fukuda and T. Kusama, *Nihon Kagaku Zasshi*, **76**, 28 (1955).

9) L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, **1946**, 235.

10) J. Turkevich, H. A. McKenzie, L. Friedman, and R. Spurr, *J. Amer. Chem. Soc.*, **71**, 4045 (1949).

11) G. V. D. Tiers, *J. Chem. Phys.*, **19**, 1072 (1951).

12) A. Amano, O. Horie, Y. Sato, and T. Katayose, *J. Jap. Petrol. Inst.*, **15**, 125 (1972).

TABLE 2. RATES OF DEMETHYLATION AND EXCHANGE OF TOLUENE-3-d_1

Temp. (°C)	H_2/reactant (mol/mol)	Residence time (s)	Conversion (mol %)		Three-halves order rate constant[a] ($l^{1/2}$ $mol^{-1/2}$ s^{-1})	
			demethylation	exchange	demethylation	exchange
677.1	5.00	8.33	3.87	4.95	0.0475	0.0613
700.7	4.97	10.84	7.95	11.50	0.0841	0.1174
	5.01	8.10	6.68	8.77		
	5.03	5.40	4.71	5.81		
	5.02	2.05	1.84	2.40		
724.6	4.92	4.03	7.09	7.94	0.1881	0.2146
	4.96	2.02	3.65	4.33		
	5.20	1.31	2.45	2.81		
750.8	5.14	2.55	9.43	10.50	0.4006	0.4874
	5.09	1.94	7.26	9.24		
	5.13	1.29	4.88	6.86		

a) Evaluated by the least-squares method for three-halves order plots of the relevant data.

TABLE 3. RATES OF DEMETHYLATION AND EXCHANGE OF TOLUENE-4-d_1

Temp. (°C)	H_2/reactant (mol/mol)	Residence time (s)	Conversion (mol %)		Three-halves order rate constant[a] ($l^{1/2}$ $mol^{-1/2}$ s^{-1})	
			demethylation	exchange	demethylation	exchange
676.3	5.06	8.30	3.54	4.19	0.0439	0.0516
	5.05	5.56	2.51	3.05		
	5.01	2.11	0.95	—		
700.4	5.07	8.05	6.48	8.51	0.0855	0.1048
	5.17	5.29	4.24	5.02		
	5.12	4.04	3.66	—		
	5.17	2.69	2.37	—		
	5.19	1.35	1.05	—		
725.6	4.95	3.94	5.82	6.70	0.1574	0.1764
	5.01	1.97	3.01	—		
	5.13	1.30	1.95	—		
750.6	5.09	1.93	6.49	7.52	0.3523	0.3935
	5.10	1.30	4.23	4.78		

a) Evaluated by the least-squares method for three-halves order plots of the relevant data.

TABLE 4. OBSERVED ACTIVATION ENERGIES, A-FACTORS AND RATES OF EXCHANGE RELATIVE TO THOSE OF DEMETHYLATION AT 700 °C

Reactant	Demethylation		Exchange		Relative rate
	E (kcal/mol)	log A	E (kcal/mol)	log A	
Toluene-2-d_1	54.0	11.12	45.0	9.27	1.45
Toluene-3-d_1	52.9	10.85	49.1	10.12	1.32
Toluene-4-d_1	53.6	10.95	51.5	10.55	1.22

three-halves order rate law for exchange (*reaction c*) as well as demethylation (*reaction b*), kinetics of the latter being in accord with those of methylbenzenes.[1] The values of $k_{1.5}$'s are then fitted into the Arrhenius formulation giving rise to the values of A-factor and activation energy (Table 4). The rate of exchange relative to that of demethylation at 700 °C, at which experiments have been carried out, is also given. The kinetic parameters of demethylation observed for three isomeric toluene-d_1's are in good agreement within error limits with each other and also with those of toluene.[12]

Kinetic Isotope Effects. Neither the secondary kinetic isotope effect nor the effect exerted by deuterium atom at different positions toward thermal demethylation has been detected. This is not surprising in view of the negligibly small effect caused by the introduction of deuterium in place of hydrogen on the electronic structure of the ring carbon atom at which substitution takes place. A similar conclusion was drawn for electrophilic nitration[13] and also for radical alkylation[14] of benzene.

Mechanism of Hydrogen-Deuterium Exchange. A similarity in demethylation (*reaction b*) and exchange (*reaction c*) with respect to the reaction order as well

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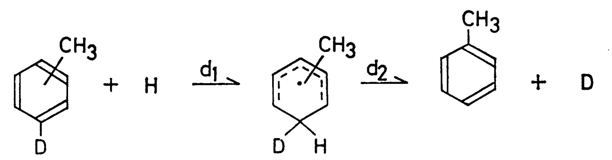
[13] W. M. Lauer and W. E. Noland, *J. Amer. Chem. Soc.*, **75**, 3689 (1953).

[14] E. L. Eliel, Z. Welvart, and S. H. Wilen, *J. Org. Chem.*, **23**, 1821 (1958).

as the values of kinetic parameters indicates that these two reactions proceed through similar pathways. Since the key reaction in the free radical chain of the demethylation is the atomic cracking (*reaction a*), the corresponding version of the exchange would be as follows.



The transient structure may be looked upon as methylcyclohexadienyl radical possessing sp^3-hybridized carbon atom which links both incoming hydrogen and outgoing deuterium. It is thus expected that the rate of *reaction d* is influenced by methyl substituent according to its position relative to deuterium in the same molecule, just as in the case of polymethylbenzenes where the demethylation rate is affected by other methyl substituents. The effect exerted by the methyl group upon *reaction d* may be conveniently correlated with S_r(R) proved to be an appropriate reactivity index for the demethylation.[1b)] Details of the definition and evaluation of the superdelocalizability values have been described.[1b)] In executing the computation, it is assumed that molecular geometry of toluene-d$_1$ is identical with that of toluene and the valence state ionization potential of deuterium atom is taken to be equal to that of hydrogen. A slight alteration in the values of these structural parameters does not affect the final results in any significant amount. As an example, 10% change in the ionization potential produces uncertainty in the fifth digit of the final S_r(R) values. The results of the extended Hückel calculation are summarized in Table 5. The linear relation obtained for the plots of logarithmic rates of the exchange relative to that of demethylation at 700 °C *vs.* the values of S_r(R) are given in Fig. 1. Other superdelocalizability values, *i.e.* S_r(E) and S_r(N), and also atomic bond population (Table 5), show no linearity with the observed reactivity ratios. This can be taken as an additional support not only for our mechanistic interpretation of the exchange reaction, but also for the use of S_r(R) as reactivity index for thermal substitutions in general. The best explanation so far for the factor influencing the reactivity of atomic cracking (*reactions* a_1 and d_1) is found in the mechanism assuming electroneutral hydrogen atom attack and rehybridization of sp^2 ring carbon atom to the sp^3-state in a concerted manner.

TABLE 5. REACTIVITY INDICES OF TOLUENE BY EXTENDED HÜCKEL METHOD

Position	Modified superdelocalizability			Atomic bond population
	S_r(R)	S_r(E)	S_r(N)	
1	0.4029	0.2749	0.5309	0.7744
2	0.4149	0.3255	0.5044	0.8243
3	0.4125	0.2836	0.5414	0.8276
4	0.4086	0.3246	0.4926	0.8276

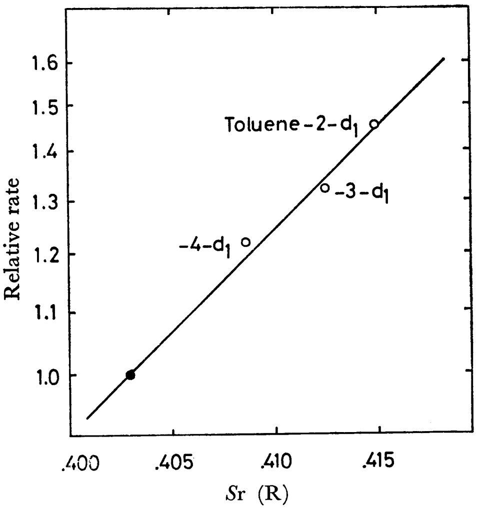


Fig. 1. Correlation between observed relative reactivity and modified superdelocalizability. ●: Demethylation, ○: Exchange.

Hydrogen Atom Addition to Aromatics and Olefins. Gas phase reactions of hydrogen atom with a series of mono-substituted benzenes have been investigated using pulse-radiolytic technique.[15)] The results indicate that the addition took place to form cyclohexadienyl-type transients, the latter presumably decomposing to benzene at higher temperatures.[16)] The rate of the adduct formation was found to obey the Hammett rule with slightly negative ρ-values (−0.7——0.8). These results suggest that the attacking hydrogen atom could be more conveniently classified as electrophilic reagent. However, according to the theoretical implications of the Hammett rule, ρ-values are by far the more sensitive towards ionic substitutions and are not suitable for classifying reactions consistently.[17)] In fact, the data available for radical alkylation of benzene give ρ-values in the range from −1.0 to +1.0. The radiolytic reactions might involve substrates with electrons populated at energy states higher than those usually encountered in thermal reactions. It is therefore possible in the former that the attacking hydrogen atom tends to be more electrophilic.

In this connection, it is interesting to refer to results reported on reactions of hydrogen atom with olefins. According to Cvetanović,[18)] the lack of parallelism between hydrogen atom and electrophilic oxygen atom in the rates of addition to a series of olefins was taken as an evidence for support of the electroneutral nature of the former. In spite of the above, hydrogen atom addition to propene, but-1-ene and isobutene has been reported as being somewhat electrophilic, based on the parallelism between the values of S_r(E) and the observed overall rates of the hydrogenolysis.[19)] Electronic be-

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15) M. Anbar, D. Meyerstein, and P. Neta, *Nature*, **209**, 1348 (1966); M. C. Sauer, Jr. and I. Mani, *J. Phys. Chem.*, **74**, 59 (1970).

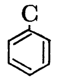
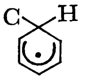
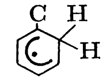
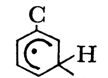
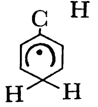
16) A. Amano, O. Horie, and N. H. Hanh, *Chemistry Letters*, **1972**, 917.

17) T. Tsuruta, T. Fueno, and J. Furukawa, *Bull. Inst. Chem. Res.*, Kyoto Univ., **34**, 214 (1956).

18) R. J. Cvetanović, "Advances in Photochemistry," Vol. 1, p. 115, Interscience, New York, 1963.

19) H. Tominaga, H. Arai, K. A. Moghul, N. Takahashi, and T. Kunugi, *Kogyo Kagaku Zasshi*, **74**, 371 (1971).

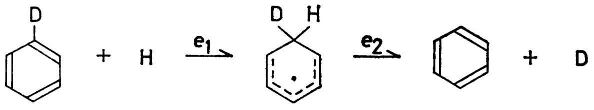
TABLE 6. THERMOCHEMICAL DATA OF THE RELEVANT SPECIES AT 700 °C

Species	ΔH_f (kcal/mol)
	44.64
	43.18
H·	55.48
CH_3·	41.81
	82.52
	80.55
	81.51
	80.87

havior of the hydrogen atom toward addition should therefore be reckonned as still controversial.

Comparison between Exchange and Demethylation. In agreement with the qualitative result obtained by Burr *et al.*,[7] we found that exchange (*reaction d*) was faster than demethylation (*reaction a*) by a factor of about 1.3. The converse would most probably be the case if elimination (*reactions* a_2 and d_2) played the rate-controlling role in the overall substitution, since *reaction* d_2 is more endothermic than *reaction* a_2 by about 14 kcal/mol. Our estimated ΔH_f values at 700 °C, based on thermochemical data (Table 6) are −16.1 and approximately −18 kcal/mol for the rate-controlling *reactions* a_1 and d_1, respectively. These values are in accord with the present results, and indicate, on the basis of LFER concept, that the tranistion-state structures for both *reactions* a_1 and d_1 resemble cyclohexadienyl transient.

According to the mechanistic analysis given quite independently by Benson *et al.* in their study of the pyrolysis of 1,3-cyclohexadiene in the presence of benzene and toluene,[20] *reaction* a_1 was found to be faster than the addition of hydrogen atom to benzene-d_6 (*reaction* e_1) by a factor of 1.5.



Reactivity ratio of *reactions* a_1 and e_1 in the range 0.3—0.7 has, however, been obtained on the hydrogen-deuterium exchange of benzene-d_1 both in the presence and in the absence of toluene. If we assume the latter ratio, the rates are in the order $d_1>e_1>a_1$. This coincides with what is expected from the calculated values of S_r(R).

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[20] S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967).