On the Mechanism of Toluene Disproportionation in a Zeolite Environment

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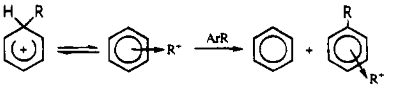
Abstract: A study of the mechanism of toluene disproportionation catalyzed by the zeolite ZSM-5 has been conducted using toluene-α,α,α-d_3. The primary mechanism is a benzylic cation chain reaction. This conclusion is deduced from the fate of the deuterium label, observation of a kinetic induction period as well as a primary kinetic isotope effect, and rate acceleration upon addition of small amounts of diphenylmethane during reaction. The magnitude of the kinetic isotope effect, 1.88 at 250 °C, implies the existence of a nearly symmetrical, linear configuration of C–H–C in the transition state of the hydride transfer step between the toluene methyl and the benzylic cation. Such a model of the transition state fits well inside the straight channel of ZSM-5, based on steric considerations alone.

Introduction

The acid-catalyzed disproportionation of alkylbenzenes to benzene and polyalkylbenzenes has been extensively investigated. Up to the present, mechanistic studies of this reaction have been carried out mainly in liquid media containing Friedel–Crafts or superacid catalysts. Early work focused on defining the reaction pathway in terms of S_N1 and S_N2 type mechanisms. These studies firmly established that transalkylations involving secondary or tertiary alkyl groups follow an S_N1 route, based on their tendency to rearrange or undergo secondary reactions on transfer.[1] Primary alkyl groups, on the other hand, do not suffer rearrangement.[1b,2] To account for this difference, McCaulay and Lien[1b] proposed an S_N2 type mechanism: Brown and Smoot[2b] later determined that the rate of

eq. 1

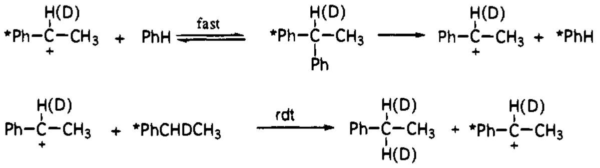
ethylbenzene disproportionation (in the presence of $AlBr_3{\cdot}HBr$) was 10^7 higher than that of toluene. This is an anomalously large difference for a direct displacement mechanism,[3] and was therefore rationalized by Brown and Smoot by invoking a "localized π-complex" intermediate in rapid equilibrium with the starting material. This interpretation was ruled out by



eq. 2

subsequent findings that for ethyltoluene (with $AlCl_3$)[4] and ethylbenzene ($AlBr_3{\cdot}HBr$),[5] transalkylation was more rapid than intramolecular isomerization, contrary to expectation from the Brown–Smoot mechanism.

A plausible solution to the enigma was provided through an elegant experiment of Streitweiser and Reif,[6] who examined the kinetics and stereochemistry of ethyl transfer from optically active ethylbenzene-α-*d*-*ring*-^{14}C to unlabeled benzene, in the presence of $GaBr_3{\cdot}HBr$. For an S_N2 reaction, the rates of inversion, k^* (from radioactivity loss), and racemization, k_{rac}, could be simultaneously determined. It was found that $k^* = k_{rac}$. This result contradicts direct displacement as a plausible mechanism, for in that case the rate of racemization would be twice that of inversion. A third alternative was therefore proposed, which was in accord with experimental observation:



$$^{*}\mathrm{Ph{-}\overset{H(D)}{\underset{+}{C}}{-}CH_3} + \mathrm{PhH} \overset{\text{fast}}{\rightleftharpoons} {}^{*}\mathrm{Ph{-}\overset{H(D)}{\underset{Ph}{C}}{-}CH_3} \longrightarrow \mathrm{Ph{-}\overset{H(D)}{\underset{+}{C}}{-}CH_3} + {}^{*}\mathrm{PhH}$$

$$\mathrm{Ph{-}\overset{H(D)}{\underset{+}{C}}{-}CH_3} + {}^{*}\mathrm{PhCHDCH_3} \xrightarrow{\text{rdt}} \mathrm{Ph{-}\overset{H(D)}{\underset{H(D)}{C}}{-}CH_3} + {}^{*}\mathrm{Ph{-}\overset{H(D)}{\underset{+}{C}}{-}CH_3}$$

eq. 3

This is a cation chain reaction involving a diphenylmethane type intermediate, or transition state. The rate determining step in this scheme is taken to be the hydride transfer between feed ethylbenzene and an α-phenethyl cation.

The mechanism of toluene disproportionation is much less well understood and has been the subject of continuing speculation. Toluene disproportionation is most effectively carried out in the gas phase in the presence of heterogeneous catalysts such as zeolites. This is the basis of an important industrial process for the synthesis of xylenes and benzene.[7] The heterogeneous environment, however, poses a serious challenge to the experimentalist attempting to unravel reaction mechanisms within its confines.

At present, two alternative mechanisms for toluene disproportionation are in favor: (1) intermolecular methyl transfer (which we denote here as **M1**), and (2) bimolecular reaction

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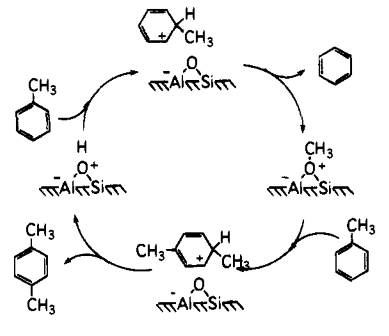
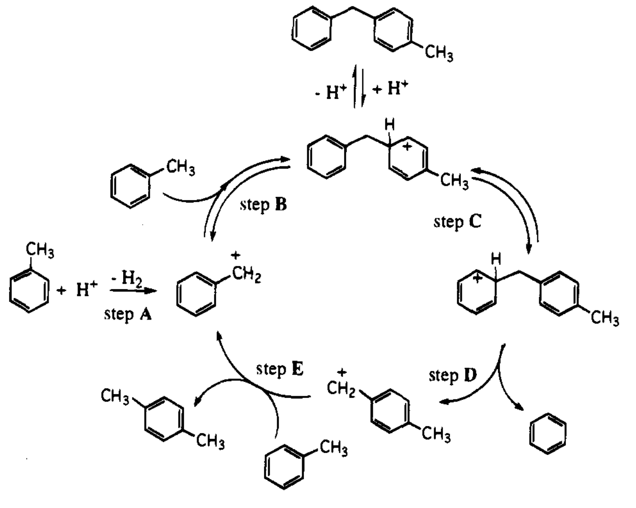
Scheme 1. M1: Methyl Transfer Mechanism



Scheme 2. M2: Diphenylmethane Mechanism



invoking a diphenylmethane-like intermediate (**M2**), after Streitweiser. These are detailed in the Schemes 1 and 2.

Up to the present, the experimental evidence in support of either mechanism has largely been derived from kinetic modeling,[8] and is at best inconclusive. Nevertheless, the majority of opinion[9] seems inclined toward mechanism **M2**, which is plausible in view of the Streitweiser result, and the well-recognized instability of the methyl cation. In this connection it should be noted that benzyl radicals (which form benzyl cations upon heating) and a diphenylmethane type cation have been detected in the zeolites mordenite, HY, and HZSM-5 by EPR and UV reflectance spectroscopy upon sorption of toluene and diphenylmethane and heating to various temperatures.[10]

We report here the results of an effort to shed further light on the mechanism of toluene disproportionation through isotope labeling, using toluene-α,α,α-d_3 as reactant. If **M1** is operative, the CD_3 will survive transfer intact. If **M2** obtains, then methyl deuterium will be partially replaced by H due to hydride chain transfer. An unavoidable complication in this approach is label scrambling. To sort out the contributions due to label scrambling is nontrivial, therefore most of the experiments are carried out under the mildest possible conditions.

Experimental Section

Equipment. Disproportionation reactions were carried out by pumping the appropriate feed, using an ISCO 500D syringe pump, into an electrically heated 0.5 in. o.d. (0.43 in. i.d.) stainless steel fixed-bed reactor, fitted with a central thermal well containing a thermocouple sensor. The catalyst bed consisted of a preheat zone (13 cm^3 of 30/60 mesh sand), a reaction zone containing 2 g of 30/60 mesh catalyst, and a post-heat zone (13 cm^3 of 30/60 mesh sand). Reaction conditions were 315 psia at various temperatures and space velocities. Hydrogen was co-fed with the hydrocarbon feed at a mole ratio of 1.0. Products were analyzed using an on-line HP 5890 gas chromatograph equipped with a 30 m, 0.25 μm DB wax capillary column and controlled by Macintosh-based laboratory automation software. Liquid products were collected at 1-h intervals for GC-MASS analysis.

GC-MASS analyses were carried out on a HP 5971A instrument equipped with a Petrocol DH 50.2 column. The ionization potential of the detector was 70 eV. Since xylene isotopomers were not fully separated on the column, selective ion chromatograms of ions having *m/e* 106 (xylene-d_0), 107, 108, and 109 were integrated to obtain the relative abundance of isotopomers. The relative ratio was adjusted for ^{13}C natural abundance and the fragmentation pattern of each xylene. Standard mass spectra for xylene-d_0, -d_1, and -d_3, obtained under the same instrument conditions, were used to correct molecular ion fragmentations. Liquid NMR analyses were done on a Brucker 360-MHz instrument using $CDCl_3$ solvent.

Catalyst. Zeolite ZSM-5[11] was synthesized according to the method of Argauer and Landolt[12] and used in the H-form.

Results and Discussion

Toluene disproportionation was carried out at 250−400 °C over a range of space velocities using a 1:9 molar ratio of toluene-α,α,α-d_3:toluene as feed. Benzene and xylenes accounted for the greater fraction of products, with the remainder consisting of higher boiling compounds such as ethyltoluene, naphthalene, and trace amounts of phenyltolylmethane. Product benzene/xylene molar ratios were approximately 1.2, and xylene isomer distributions were near equilibrium, even at the lowest conversions examined. Furthermore, deuterium distributions of the three isomers were essentially identical; accordingly, data reported below will be for *o*-xylene, as representative of total xylenes. Under conditions of this study, xylenes with deuterium content higher than d_3 are generally low ($<10\%$ of d_3), and will be disregarded.

Table 1 lists the *o*-xylene isotopomer distributions as determined by GC-MASS. Included for reference are the theoretical distributions for four limiting cases (1:9 toluene-d_3:toluene feed): diphenylmethane mechanism (**M2**), methyl transfer mechanism (**M1**), label scrambling (CH_3 only), and label scrambling among all positions. Runs 1a and 1b are replicates, as are 2a and 2b.

The results from Runs 1−3, obtained at low ($<3\%$) conversion, appear in general to support the **M2** mechanism, based on a gross similarity to the calculated **M2** deuterium distribution. However, it also appears that at these low conversion levels the observed d_2:d_3 ratios of 0.44−0.81 are generally below the expected value of 0.9 for a pure **M2** mechanism. This cannot be attributed to concurrent label scrambling, since this would result in an increase in the ratio. In Figure 1, a plot of the variation of xylene isotopomer distribution with contact time is presented. Here the greatest change is seen to be in the concentration of d_3 isotopomer, which declines with increasing contact time. The d_2 and d_1 isotopomers appear to be forming at the expense of d_3. The data are generally suggestive of a contribution from an **M1** mechanism, if d_3 is largely associated

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[8] For example: (a) Gnep, N. S.; Guisnet, M. *Appl. Catal.* **1981**, *1*, 329. (b) Nayak, V. S.; Riekert, L. *Appl. Catal.* **1986**, *23*, 403. (c) Beltrame, P.; Beltrame, P. L.; Carniti, P.; Forni, L.; Zuretti, G. *Zeolites* **1985**, *5*, 400. (d) Bhaskar, G. V.; Do, D. D. *Ind. Eng. Chem. Res.* **1990**, *29*, 1814. (e) Dooley, K. M.; Brignac, S. D.; Price, G. L. *Ind. Eng. Chem. Res.* **1990**, *29*, 789; (f) Uguina, M. A.; Sotelo, J. L.; Serrano, D. P. *Ind. Eng. Chem. Res.* **1993**, *32*, 49.

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[11] Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

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Table 1. Product Xylene Isotopomer Ratio in Toluene Disproportionation Over HZSM-5/SiO_2 (1:9 Toluene-d_3/Toluene Feed)

	temp, °C	WHS h^{-1}	conv, %	xylene-d_0	xylene-d_1	xylene-d_2	xylene-d_3
diphenylmethane mech.				8.10	0.90	0.90	1.00
methyl transfer mech.				4.50	0.00	0.00	1.00
scrambled (among CH_3)				36.4	24.3	6.74	1.00
scrambled (including ring H)				302	94.1	12.8	1.00
run 1a	250	3.00	0.20	7.90	1.03	0.44	1.00
run 1b	250	3.00	0.20	7.28	0.87	0.45	1.00
run 2a	250	1.50	0.58	11.39	0.97	0.52	1.00
run 2b	250	1.50	0.53	10.87	0.90	0.47	1.00
run 3	250	0.375	2.36	13.60	1.49	0.81	1.00
run 4	250	0.188	6.17	19.30	2.62	1.21	1.00
run 5	250	0.094	14.7	39.14	7.82	2.32	1.00
run 6	300	3.00	0.16	26.00	4.02	1.55	1.00
run 7	340	3.00	4.9	103.69	29.82	5.08	1.00
run 8	250	3.00	0.1	24.70	1.58	0.67	1.00
run 9	300	3.00	1.0	72.55	5.76	1.39	1.00
run 10	340	3.00	3.3	226.83	30.52	2.78	1.00
run 11	400	3.00	16	354.52	95.43	10.95	1.00

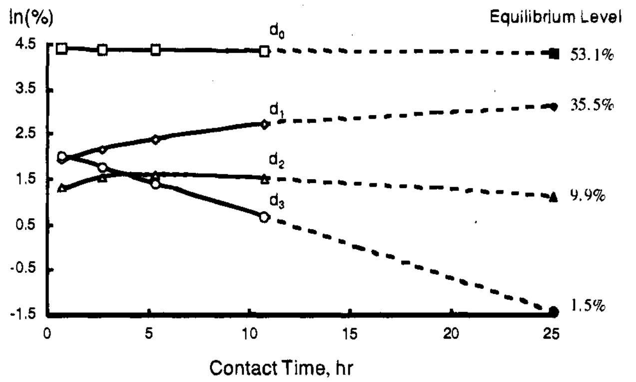

Figure 1. Xylene isotopomer percentage vs contact time from Runs 1−5.

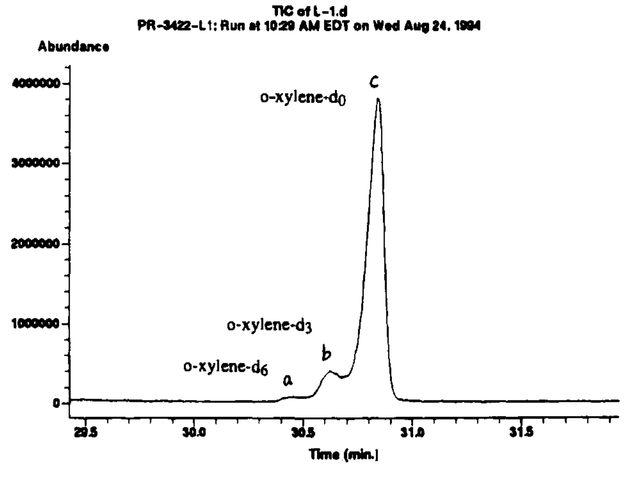

Figure 2. GC (TIC) of the *o*-xylene portion from Run 2a.

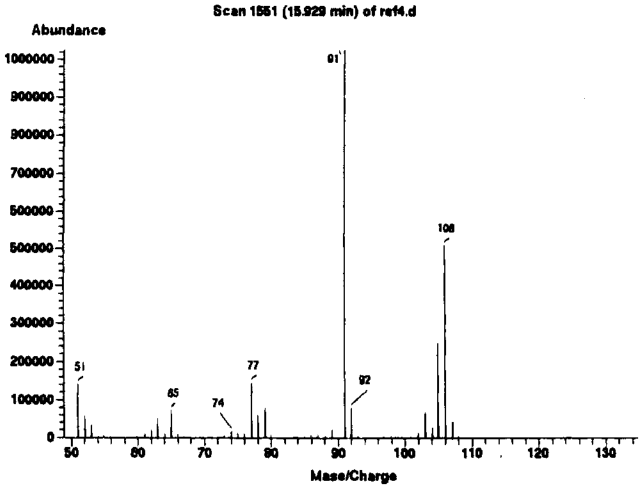

Figure 3. MASS spectrum of *p*-xylene-d_0.

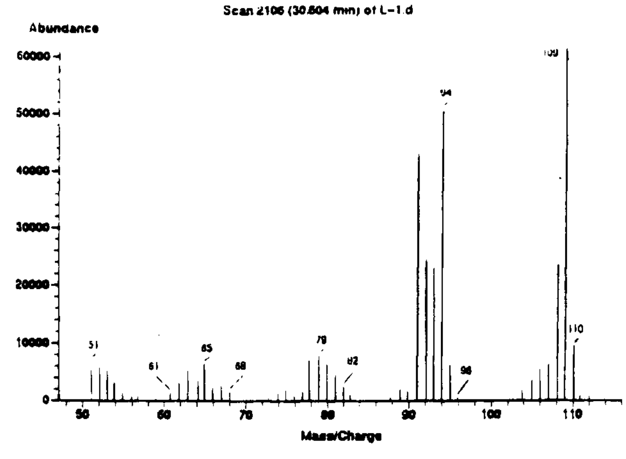

Figure 4. MASS spectrum of *o*-xylene-d_3, peak **b** in Figure 2.

with the methyl group. This was confirmed by GC-MASS. At low reaction temperature and conversion, the deuterium distribution in xylene-d_3 was indeed found predominantly in the methyl positions, as exemplified by the data in Figures 2−4 from Run 2a. The GC (TIC chromatograph) of the *o*-xylene fraction is shown in Figure 2. The d_3 isotopomer (peak **b**) is well-resolved because of the low levels of d_1 and d_2. Figure 4 shows the MASS spectrum of peak **b**. This is almost identical to data of Figure 5, MASS spectrum of an authentic sample of xylene-α,α,α-d_3. The MASS spectrum of nondeuterated *p*-xylene under the identical instrument conditions is shown in Figure 3 to illustrate the similar fragmentation pattern of xylene isotopomers. Thus the observed high relative level of xylene-d_3 isotopomer derives from intact CD_3, supporting the possibility of a contribution from process **M1**, at least at low conversions. Owing to the aforementioned instability of the methyl cation, a direct ring-to-ring transfer would be unlikely. It is likely that the zeolite framework may play an intermediary role as a methyl

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(13) (a) Hellring, S. D.; Schmitt, K. D.; Chang, C. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1320. (b) Aronson, M. T.; Gorte, R. J.; Farneth, W. E. *J. Catal.* **1987**, *105*, 455. Kubelkova, L.; Novakova, J.; Nedomova, K. *J. Catal.* **1990**, *124*, 441. (c) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840. (d) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2025. (e) Bosacek, V. *J. Phys. Chem.* **1993**, *97*, 10732.

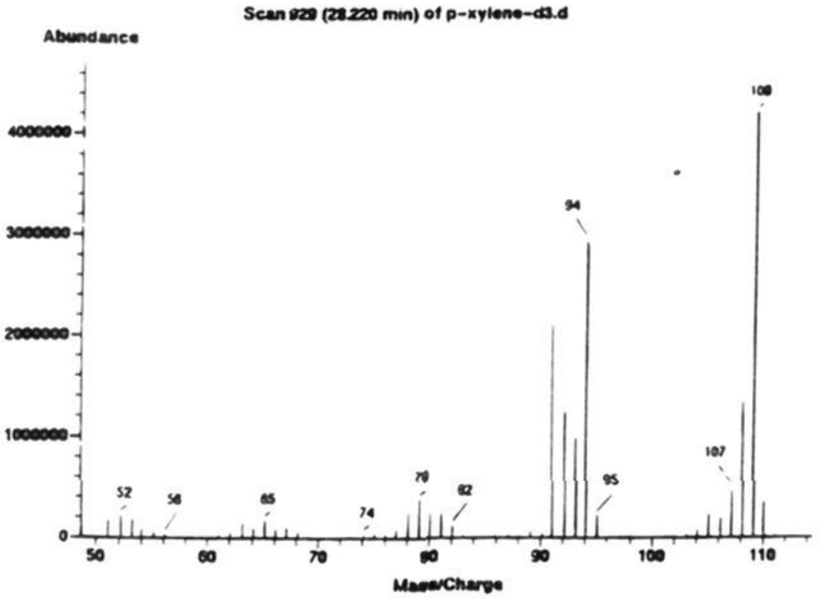

Figure 5. MASS spectrum of p-xylene-α,α,α-d_3.

Table 2. Kinetic Isotope Effect on Xylene Isotopomer Ratio According to **M2**

PKIE (k_H/k_D)	xylene-d_0	xylene-d_1	xylene-d_2	xylene-d_3
1.0	8.1	0.9	0.9	1
1.5	8.6	0.64	0.64	1
2.0	8.8	0.49	0.49	1
2.5	8.8	0.39	0.39	1
2.8	8.9	0.35	0.35	1

shuttle, via formation of methoxy- or methyloxonium-ZSM-5, which are known derivatives of the zeolite.[13]

The dominant H−D exchange processes at the early stages of the reaction are $d_0 + d_3 \rightarrow d_1 + d_2$ and $d_0 + d_2 \rightarrow 2d_1$. This accounts for the generally higher levels of d_1 relative to d_2 observed. Thus at 250 °C and low conversions label scrambling is still quite significant. At higher conversions (>2%), the relative amounts of d_1 and d_2 isotopomers to d_3 increase beyond the level predicted for the **M2** mechanism due to label scrambling, which begin to obscure the effects of transalkylation on H−D distribution. Therefore the observed high levels of d_1 and d_2 relative to d_3 cannot be attributed simply to a higher proportion of **M2** relative to an **M1** process, if both mechanisms operate.

Turning now to the **M2** mechanism, scission of the C−H σ-bond occurs twice in the cycle (steps A and E), therefore a primary kinetic isotope effect (PKIE) might be expected. Depending on its magnitude, a PKIE may have a significant influence on the observed deuterium distribution. An estimation of these effects is given in Table 2, where it is seen that an increase in the PKIE is reflected, *inter alia*, in a decrease in the d_2:d_3 ratio. This effect, therefore, could also be a cause of the low d_2:d_3 ratios at low conversion.

An experimental determination of the PKIE was carried out using toluene-d_8 as reactant. Figure 5 shows the pseudo-first-order plots for the reactions of deuterio- and protiotoluene at 250 °C. It can be seen that after an initial induction period (presumably due to step A), the kinetics are first order in toluene. The kinetic isotope effect, k_H/k_D, is obtained from Figure 6 as 1.88. The calculated xylene isotopomer distributions d_0:d_1:d_2:d_3 are 8.8:0.49:0.49:1 based on the **M2** mechanism only. These numbers fit experimental data of Runs 1a and 1b equally as well as assuming dual **M1** and **M2** mechanisms. The higher than calculated values for d_0 and d_1 are the result of isotope exchange processess which eventually scramble the isotope among all hydrogen positions at longer contact times.

This is an unexpectedly large PKIE in view of the high reaction temperature (the theoretical upper limit for the PKIE at 250 °C is 2.8[14]). It has been well-established that in H-transfer reactions, the PKIE is maximized for symmetrical, linear transition states.[15] Here, "linearity" connotes colinearity of the migrating H between its origin and terminus, not necessarily of configurations of the two molecules involved.

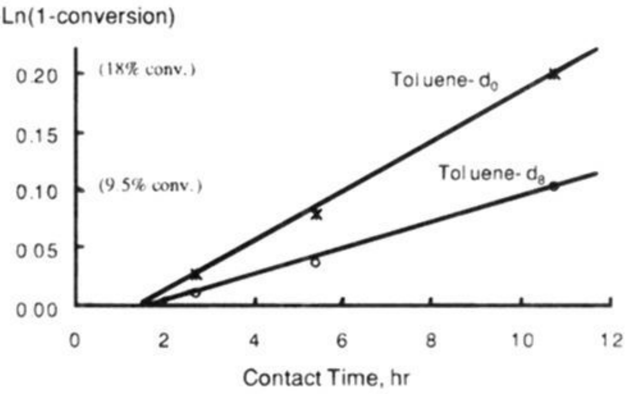

Figure 6. Kinetics of toluene disproportionation at 250 °C, toluene-d_0 vs toluene-d_8.

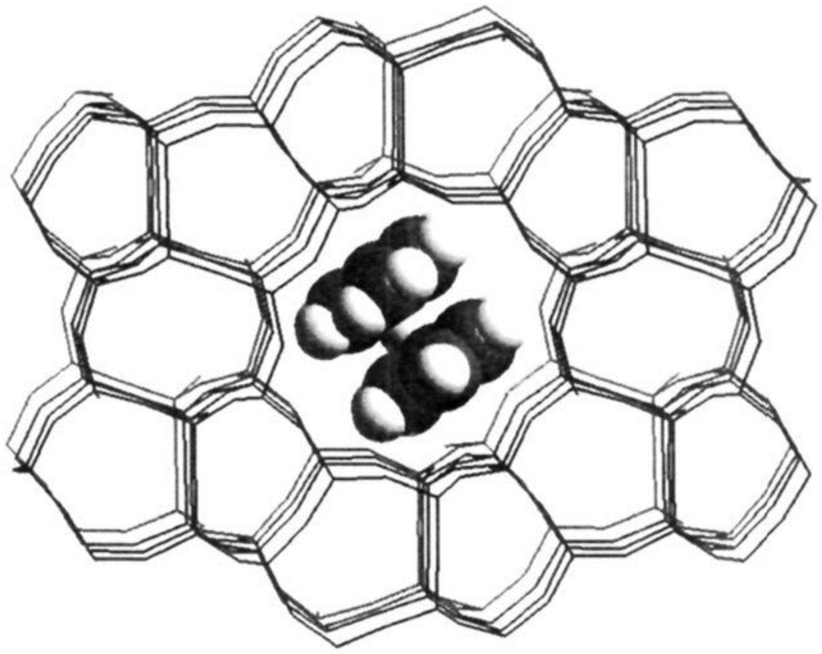

Figure 7. Cerius model of benzyl cation + toluene transition state in ZSM-5 straight channel.

In toluene disproportionation over HZSM-5, such a large kinetic isotope effect can only be associated with a hydride transfer process step E in **M2** mechanism. (Although diarylmethanes may be a better hydride donor than toluene, their low concentration and diffusivity in zeolite environment does not allow them to compete with toluene.) A CPK model of the transition state assuming a configuration of linear C−H−C arrangement, a 90° angle between the partial C−H bond and phenyl−methyl bond, and a partial bond distance[16] of 1.25 Å fits snugly in the straight channel of ZSM-5 (Figure 7). Such a crude model can only be used to show a possible configuration invoking steric interactions alone. The true transition state configuration undoubtedly deviates from that shown in Figure 7 because of interactions with the zeolite wall, and with framework counterions. The current results can be seen as a good example of Csicsery's proposed "restricted transition state shape selectivity".[17]

In accordance with the **M2** mechanism, the diphenylmethane species would be key intermediates, as precursors to benzylium chain transfer agents. An experiment cofeeding small amounts

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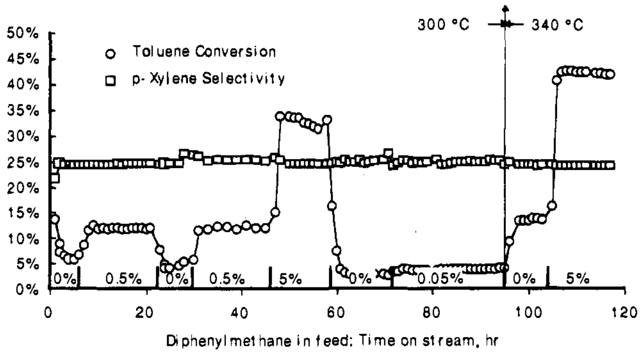

Figure 8. Toluene disproportionation in the presence of diphenylmethane (WHSV 2.0).

of diphenylmethane with toluene was carried out to determine if conversion of toluene is affected. Results are summarized in Figure 8, a chronology of a continuous run during which various amounts of diphenylmethane were introduced and withdrawn.

The rate acceleration due to the presence of diphenylmethane is clearly evident, and highly reproducible. At 300 °C and 2.0 WHSV, toluene conversion increased from 2.8% to 3.8% with 0.05% of diphenylmethane and to 11.8% with 0.5% of diphenylmethane. Product analyses indicated essentially quantitative (>98%) consumption of diphenylmethane: At 5% diphenylmethane feed, 0.03% of the diphenylmethane and 0.05% of the phenyltolylmethane were detected in the liquid stream. The product benzene/xylene ratio also increased from 1.1 to 1.3, as expected from the coversion of diphenylmethane to benzene and benzylic cation. While product analyses support the intermediacy of diarylmethane in toluene disproportionation, the sensitivity of toluene conversion toward addition of diphenylmethane further indicated the nature of a chain reaction: Addition of diphenylmethane removes the induction period and perhaps increases the concentration of chain carriers such as protonated diarylmethane and benzylic cations.

Conclusions

The experimental evidence presented herein clearly supports an **M2** "diphenylmethane" mechanism for toluene disproportionation in HZSM-5. This conclusion is based on the results of deuterium labeling, observation of a kinetic isotope effect, and rate enhancement due to introduction of small amounts of diphenylmethane. The presence of an induction period is also consistent with the **M2** scheme, as is the detection of trace amounts of phenyltolylmethane in the products. The observed $k_H/k_D = {\sim}2$ at 250 °C is large, and indicates a near symmetrical, linear configuration of C−H−C in the transition state for step E. Based on steric considerations only, the proposed transition state fits snugly inside the straight channel of ZSM-5. One can predict that with larger-pore zeolite, the kinetic isotope effect in toluene disproportionation will likely be larger because the transition state can adopt a configuration closer to the symmetric, linear configuration of C−H−C. On the other hand, for a bulkier molecule such as xylene or trimethylbenzene, disproportionation will likely display a smaller kinetic isotope effect.

Finally all current experimental results can be accounted for by the **M2** mechanism. The **M1** mechanism is therefore not requisite, though it cannot be excluded as a competitive process in the early stages of reaction.

Acknowledgment. The authors are grateful to Dr. Ahmad Moini for assistance in generating the Cerius Model of the transition state for hydride transfer between benzyl cation and toluene in ZSM-5.

Supporting Information Available: Preparation of *p*-xylene-α-d_1, *p*-xylene-α,α-d_2, and *p*-xylene-α,α,α-d_3; calculation of xylene isotopomers ratio based on M2; run data for calculating kinetic isotope effect in toluene disproportionation using toluene-d_0 and toluene-d_8 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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