JOURNAL OF CATALYSIS 111, 146–151 (1988)

Toluidine Isomerization by HZSM-5

RITA H. HARDY AND BURTRON H. DAVIS

Kentucky Energy Cabinet Laboratory, P.O. Box 13015, Lexington, Kentucky 40512

Received April 27, 1987; revised December 23, 1987

The isomerization of alkylaromatics has been widely studied. Early investigations with "homogeneous catalysts," for example, metal halide–hydrogen halide complexes in aromatic solvents, established that the major reaction pathway utilized a series of 1,2-alkyl shifts (*1–5*). Tracer studies with homogeneous catalysts indicated that methyl groups migrated on a ring in an intramolecular mechanism rather than by a series of intermolecular methyl migrations (*6, 7*). On the other hand, alkyl groups more complex than the methyl group—ethyl, *n*- or isopropyl, *t*-butyl, etc.—appeared to isomerize by intermolecular shifts (*7–9*).

With amorphous silica alumina (*10*), the series of 1,2-methyl shifts was the dominant reaction pathway although the apparent selectivity for this mechanism was lower than that obtained with the homogeneous catalyst. With the larger-pore zeolite, LaY, the apparent deviation from the 1,2-methyl shift mechanism was even greater than that for amorphous silica–alumina catalysts (*11, 12*).

With an intermediate-pore-size zeolite, HZSM-5, xylene isomerization appeared to be nonselective since the primary products consisted of essentially an equilibrium mixture (*13*). However, recent tracer studies utilizing [1-^{13}C]toluene have shown that the dominant reaction pathway for methyl migration in toluene, a reactant less susceptible to diffusion disguise than the xylene isomers, is by a series of 1,2-methyl shifts (*14*).

It was of interest to compare the alkyl migration of a methyl substituent in the presence of a heteroatom-substituted aromatic to the results obtained for dialkyl aromatics. In this study, the isomerization of toluidine was investigated using an HZSM-5 catalyst.

EXPERIMENTAL

The isomerization reactions were performed in a plug flow reactor using approximately 1 g of an HZSM-5 catalyst. The ammonium acid form of ZSM-5, obtained from Mobil Research and Development Corp., was calcined at 550°C prior to use. A 1% solution of toluidine(s) in benzene was passed through the reactor at flow rates ranging from 1 to 60 ml/hr.

The temperature of the reactor was maintained at 400°C. During a run, the system was allowed to stabilize for each flow rate, the material collected during the stabilization period was discarded, and a minimum of two 2-cc liquid samples was collected.

The products were analyzed by gas chromatography with a flame ionization detector using a 60 M × 0.32-mm (i.d.) carbowax capillary column. Capillary gas chromatography–mass spectrometry was utilized to identify minor components.

After each run, the catalyst was regenerated by flushing the system with air and increasing the temperature to 500°C. The system was maintained at this temperature for at least 4 hr. The reactor was then cooled to reaction temperature and flushed with nitrogen for 1 hr prior to the next run.

Toluidine isomers were converted over HZSM-5 catalyst at 400°C. Disproportionation to aniline was a minor reaction pathway as compared to the isomer interconversions. Disproportionation becomes

0021-9517/88 $3.00

TABLE 1

Compositions Reported for Equilibrium Mixture of Toluidine Isomers

Reference	Toluidine		
	ortho	*meta*	*para*
API	6.3	3.2	90.5
Weigert (*16*)	31	52	17
Arpe and Litterer (*17*)[a]	18.6	50.4	29.2
This study	33.7	50.2	16.1
Xylenes (*13*)	23	53	24

[a] Toluidine composition after 16 hr at 400°C in contact with ZSM-5 using 100% *para*-toluidine feed.

significant only after a near equilibrium amount of toluidines is formed. It appears that at the same fractional approach of the reactant isomer to an equilibrium composition, all three isomers undergo disproportionation to the same extent. Only trace amounts of dimethylanilines were observed, even at the highest toluidine conversions. Aniline, a product of disproportionation, was less than 4 mole% of the nitrogen compounds at 80% approach to the equilibrium composition for all three reactants. The benzene solvent was essentially unreactive under these conditions; only small amounts of a compound of m/z 168, thought to be methylbiphenyl, was formed.

The equilibrium composition of the three isomers was calculated using free energies of formation (ΔG_f) reported by API (*15*). At 400°C, the calculated composition is 6.3% *ortho*, 90.5% *para*, and 3.2% *meta*. However, experimental data showed the equilibrium composition to be 33.7% *ortho*, 50.2% *meta*, and 16.1% *para*; this composition agrees with the data of Weigert (*16*) and Arpe and Litterer (*17*). This composition is similar to other methyl-substituted benzene systems such as the xylenes and cresols (*18, 19*). To verify the equilibrium composition more accurately, a near equilibrium composition (based on this run and Refs. (*16, 17*)) was prepared and passed through the reactor system. Temperature was held at 400°C and flow rates were varied as in previous runs. GC analysis of these products showed the initial composition to consistently shift to the equilibrium composition that contains 33.7% *ortho*-xylene rather than the calculated one with 6.3% *ortho*-xylene. The experimental equilibrium data obtained in this study agree very closely with the composition obtained by Weigert as well as one reported by Arpe and Litterer (*17*). Included in Table 1 is the equilibrium composition for the three xylene isomers. The similarity of the xylene isomerization composition and the experimentally determined toluidine compositions suggests that the equilibrium value calculated from the API data is incorrect. In any event, a similar set of relative rate constants will be calculated using the Wei and Prater method for the toluidine equilibrium concentrations given in Table 1 except for the API data.

The Wei and Prater technique (*20*) was employed to calculate a set of six relative rate constants for the isomerization of toluidines over HZSM-5 catalyst. This technique is well suited to calculating kinetic data for reversible monomolecular systems. In performing these calculations, the toluidine compositions are mathematically transformed to chemically fictitious species which follow unimolecular, uncoupled kinetics.

An initial isomer composition of 24.7% *para*-toluidine and 75.3% *meta*-toluidine resulted in a straight line reaction path to the equilibrium point. Using this information, two additional straight line paths were calculated defining two of the four quandrants on the reaction simplex. The data from four experimentally determined reaction paths falling within these two quandrants (feed composition of 100% *meta*; 100% *para*; 80% *para*, 20% *ortho*; or 60% *para*, 40% *meta*) were used to calculate rate constants by the Wei and Prater technique. The resulting four sets of rate constants were similar. Calculated reaction line paths for each

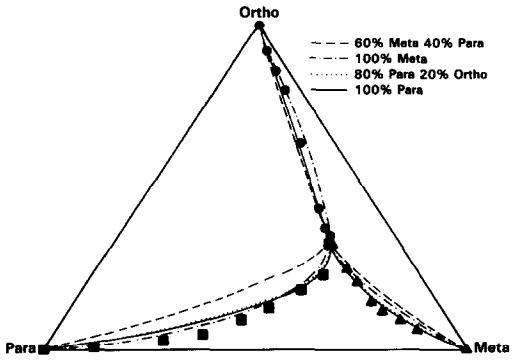


FIGURE 1

of the four sets of rate constants are shown in Fig. 1. The rate constants from the 100% *para*-toluidine data gave the best overall fit to the experimental data. These relative rate constants are given in Table 2. Shown in Fig. 2 are calculated curves using the kinetic constants from the pure *para*-toluidine curved line reaction path; the experimental data are represented by points.

The approach of toluidine isomerization to equilibrium is presented as a function of total conversion of the pure toluidine reactant in Figs. 3A through 3C. From plot 3B, it is shown that the *meta* isomer is converted to the *para* isomer at a faster rate than it is converted to the *ortho* isomer. *para*-Toluidine attains its equilibrium composition at approximately 30% *meta*-toluidine conversion. The conversion of *para*-toluidine to the *meta* isomer is relatively fast and reaches the equilibrium composition at 60% conversion. On the other hand, conversion of the *para* isomer to *ortho*-toluidine is initially very low. The conversion of *ortho*-toluidine to *meta*-toluidine and *para*-toluidine does not follow the above trend since the approaches to equilibrium of both the *para*- and *meta*-toluidine appear to be almost equal.

TABLE 2

Wei and Prater Relative Rate Constants

Rate Constants	HZSM-5 at 400°C	Weigert	
ortho → *meta*, K_{21}[a]	4.19	1.7[b]	(4.79)[c]
meta → *ortho*, K_{12}	2.82	1.0	(2.82)
para → *meta*, K_{23}	11.07	10.2	(28.76)
meta → *para*, K_{32}	3.40	3.3	(9.31)
para → *ortho*, K_{13}	2.19	0	
ortho → *para*, K_{31}	1.00	0	

[a] 1, *ortho*, 2, *meta*, and 3, *para* isomers; thus, K_{21} corresponds to 1 → 2 (*ortho* → *meta*).

[b] As reported in Ref. (*16*).

[c] Calculated to make K_{12} the same for both data sets.

TABLE 3

Reactant	Selectivity	HZSM-5 approach to equilibrium (low conversion)	Wei and Prater
para-Toluidine	*meta*/*ortho*	4.6	5.0
meta-Toluidine	*ortho*/*para*	0.4	0.8
ortho-Toluidine	*meta*/*para*	1.1	4.2

Conversion selectivity ratios for each toluidine reactant were estimated by taking the ratio of the slope of approach to equilibrium curves and by comparing the relative rates generated by the Wei and Prater technique. These selectivities are reported in Table 3. The same trend is obtained whether the Wei and Prater approach or the aproach to equilibrium plots is utilized to obtain the selectivity data.

At the higher conversions of each of the three toluidine reactants, a side reaction became significant. One of the products from this secondary reaction is aniline. For each

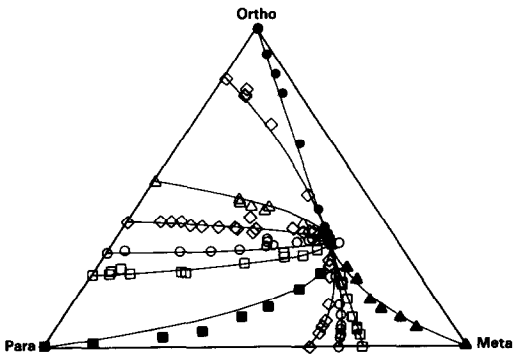


FIGURE 2

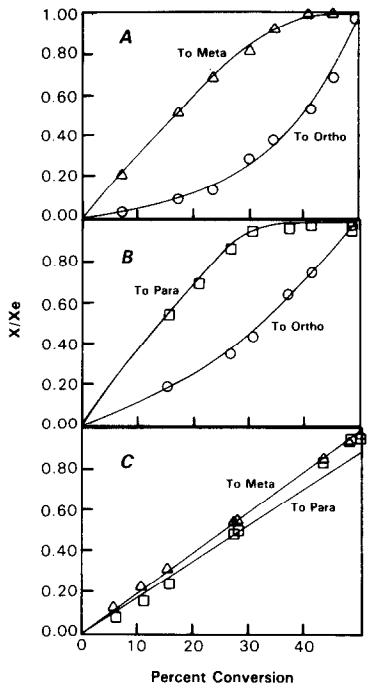


FIGURE 3

of the three reactants, less than 4 mole% of aniline is formed below a conversion that corresponds to about 80% approach to equilibrium for that isomer. At higher conversions this secondary reaction becomes extensive and 30% or more aniline may be formed. A second component was formed along with aniline. Gas chromatography–mass spectrometry was utilized to confirm the identity of aniline and the second component, a methylbiphenyl. As shown in Fig. 4, the amount of methylbiphenyl is directly related to the amount of aniline over the total conversion range observed in this study. The data, as plotted, are for the relative GC area percentage adjusted for the difference in molecular weight but not for the difference in GC response factor. Considering this, the slope of ca. 1.2 to 1.4 is consistent with the formation of essentially the same number of moles of aniline and methylbiphenyl over the total conversion range; furthermore, this selectivity does not appear to change when the higher conversions are attained.

HZSM-5 does have catalytic activity for the isomerization of toluidines. Under similar reaction conditions, LaY had essentially no catalytic activity for toluidine isomerization or the activity was masked by a very rapid poisoning–coking process. Furthermore, transalkylation contributed little to the conversion of any of the three isomers until a particular isomer had undergone 80% or greater conversion to other toluidine isomers.

The Wei and Prater method should provide a set of relative rate constants that fit a number of experimental curved reaction paths. However, in this reaction system it is not a simple procedure to obtain a set of relative rate constants. As shown by the curves in Fig. 1, simply determining a curved line reaction path for a single pure reactant may not provide a very satisfactory set of relative rate constants. However, it is apparent from the data in Table 2 that the relative rate constants calculated by Weigert (*16*), using a gear iterator to calculate rate constants for this reaction system, are similar to those obtained by the Wei and Prater technique. Thus, the Wei and Prater method appears to be as applicable to this heteroatom system as it was to the alkyl aromatic system.

The conversion selectivity of the *para*-toluidine isomer is that which is expected for an isomerization mechanism that involves a series of 1,2-methyl (or NH_3^+)

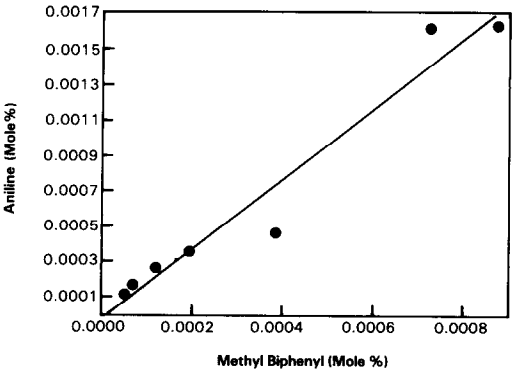
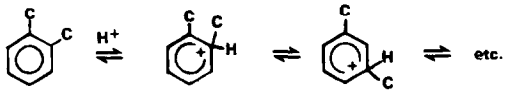


FIGURE 4

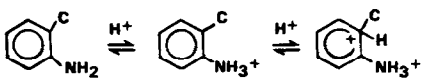
shifts since the only, or predominate, initial product is *meta*-toluidine; the concentration of *ortho*-toluidine appears to approach a small, or zero, value for low conversion of *para*-toluidine (Fig. 3A). For *meta*-toluidine, *para*-toluidine appears to be the dominant initial product (Fig. 3B) and could be consistent with a 1,2-methyl shift. For *ortho*-toluidine conversion, both *meta*-toluidine and *para*-toluidine are formed in essentially equal amounts during conversions up to 60% of the reactant (Fig. 3C). For the *ortho* isomer, either a 1,2-methyl shift does not operate or a more rapid diffusion of the *para* isomer introduces diffusional disguise into the kinetic picture. Diffusional disguise would also explain the greater production of the *para* isomer over the *ortho* isomer when *meta*-toluidine is the reactant. The relative rate constants (Tables 2 and 3) as well as the selectivity plots in Figs. 3A, 3B, and 3C suggest that the dominant isomerization mechanism is a series of 1,2 shifts with a superimposed disguise that provides a favored pathway for enhanced production of *para*-toluidine during the kinetic measurements.

Acid-catalyzed isomerization of xylene is usually considered to involve protonation of the ring followed by methyl migration to produce a protonated alkyl aromatic isomer:



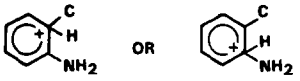
(1)

Deprotonation of the alkyl aromatic provides the isomerized product. It is difficult to explain toluidine isomerization by a similar mechanism. The first proton should add to the much more basic NH_2 group; once the toluidinium ion is formed, it is unlikely that a second proton will add to form the higher (2+) charged species:



(2)

The 2+ species appears more likely than the protonation of the ring while the much stronger base, NH_2, remains unprotonated:



(3)

If it is proposed that the 2+ species shown in (2) is formed, one has the problem of explaining how the toluidine was able to acquire two protons in the channel of a low-alumina, low-proton-density zeolite HZSM-5. It appears that the formation of structure (2) requires migration of the toluidinium ion, or at least one proton, over a considerable distance. Furthermore, if negative charges remain localized at the zeolitic site with a framework alumina, the 2+ charge of the aromatic species must be counterbalanced by two negative charges, at least one of which must be separated by a significant atomic distance from the organic cation.

If the 2+ species is accepted as an intermediate in the isomerization mechanism, it is then speculated that the isomerization of toluidine is analogous to that of xylene, with one exception. In the case of toluidine, one of the side-chain groups is the charged NH_3^+ group rather than CH_3 and the CH_3, not NH_3^+, migrates in the toluidine isomerization mechanism. Deprotonation of the above toluidines then provides the isomerized products.

Attempts were made to isomerize picolines. In one run, a feed containing 1% *ortho*-picoline in benzene was passed over the catalyst and, and even at the lowest flow rate used in the current study, no conversion products could be detected. The benzene/picoline feed was terminated and immediately replaced by a 1% *ortho*-toluidine in benzene solution. The toluidine underwent conversion at a level similar to that obtained with a catalyst that had never been exposed to picoline; thus, the ZSM-5 catalyst was active and was not permanently poisoned by the picoline. The feed was subsequently changed to 1% picoline in

benzene and again there was no detectable conversion. A similar result was obtained with 1% *para*-picoline except the first liquid condensing from the reactor contained a small quantity of *ortho*-picoline but no detectable quantity of *meta*-picoline. These results indicate that picolines are isomerized much more slowly than the corresponding toluidine isomer. Unless there is considerably more charge stabilization by the NH_3^+ group of protonated toluidine than that by the NH^+ when nitrogen is in the ring, the difference in the extent of conversion of the two compound classes suggests that toluidine isomerization occurs by migration of NH_3^+ rather than by a 2+ species.

The "disproportionation" to form methylbiphenyl and aniline is a complex reaction that involves even oxidation–reduction; it extends data interpretation too far to write a detailed mechanism for this reaction at this time.

ACKNOWLEDGMENTS

This work was performed at the Kentucky Energy Cabinet Laboratory (KECL) with funding from the Commonwealth of Kentucky, Kentucky Energy Cabinet. The KECL is administered under contract by the University of Louisville. We also acknowledge very fruitful discussions with Dr. F. W. Weigert and the then unpublished results that he shared with us.

REFERENCES

1. McCauley, D. A., and Lien, A. P., *J. Amer. Chem. Soc.* **74,** 6246 (1952).
2. Brown, H. C., and Jungk, H., *J. Amer. Chem. Soc.* **77,** 5579 (1955).
3. Allen, R. H., and Yates, L. D., *J. Amer. Chem. Soc.* **81,** 5289 (1959).
4. Brown, H. C., and Smoot, C. R., *J. Amer. Chem. Soc.* **78,** 2176 (1956).
5. Collins, D. J., Scharff, R. P., and Davis, B. H., *Appl. Catal.* **28,** 35 (1986).
6. Steinberg, H., and Sixma, F. L. J., *Recl. Trav. Chim. Pays-Bas,* **81,** 185 (1962).
7. Roberts, R. M., and Roengsumran, S., *J. Org. Chem.* **46,** 3689 (1981).
8. Allen, R. H. Alfrey, T., Jr., and Yates, L. D., *J. Amer. Chem. Soc.* **81,** 42 (1959).
9. Roberts, R. M., and Douglass, J. E., *Chem. Ind.,* 155 (1958).
10. Silvestri, A. J, and Prater, C. D., *J. Phys. Chem.* **68,** 3268 (1964).
11. Collins, D. J., Mulrooney, K. J., Medina, R. J., and Davis, B. H., *J. Catal.* **75,** 291 (1982).
12. Chutoransky, P., and Dwyer, F. G., *Adv. Chem. Ser.* **121,** 5k40 (1973).
13. Collins, D. J., Medina, R. J., and Davis, B. H., *Canad. J. Chem. Eng.* **61,** 29 (1983).
14. Dabbagh, H., Dadey, E., and Davis, B. H., *J. Catal.* **109,** 232–235.
15. Kudchadker, A. P., Kudchadker, S. A., and Wilhoit, R. C., *API Publ. 720,* (1982).
16. Weigert, F. J., *J. Org. Chem.* **52,** 3296 (1987).
17. Arpe, H. J., and Litterer, H., Eur. Patent Appl. EP 92,103 (Oct. 26, 1983); *Chem. Abstr.* **100,** 6057d (1984).
18. Taylor, W. J., Wagman, D. D., Williams, M. G., Ditzer, K. S., and Rossini, F. D., *J. Res. Natl. Bur. Stand.,* Res. Paper RP1732, **37,** 95 (1946).
19. Hastings, S. H., and Nicholson, D. E., *J. Chem. Eng. Data* **6,** 1 (1961).
20. Wei, J., and Prater, C. D., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 13, p. 203. Academic Press, New York, 1962.