

Isomerization of Methylbenzonitriles Catalyzed by HZSM-5

Frank J. Weigert

Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Received October 22, 1985

The zeolite HZSM-5 catalyzes methyl migration in toluonitriles and dimethylbenzonitriles by intramolecular 1,2-shifts. Only the three dimethylbenzonitriles with the 1,2,4-substituent pattern are small enough to take part in the shape selective reaction.

Acid-catalyzed methyl migration is practiced on a billion-pound scale for the manufacture of *p*-xylene.¹ Both the intermolecular disproportionation reaction of toluene and the intramolecular isomerization of the three xylene isomers are important reactions. The zeolite HZSM-5 is selective for the intramolecular reaction.²

Other substituted toluenes have also been isomerized. Olah studied the isomerization of chloro- and bromo-toluenes³ with $\text{AlCl}_3/\text{H}_2\text{O}$ catalysts. Both cresols⁴ and toluidines⁵ have been isomerized with HZSM-5 catalysts. All of these substituted toluenes have substituents which are ortho/para directing, although the halides are electron withdrawing.

In this paper, I describe the HZSM-5-catalyzed intramolecular isomerization of toluonitriles and selected dimethylbenzonitriles (DMB's). The reactions serve to demonstrate three types of zeolite selectivity: reactant, transition state, and product.

Results

Passing individual toluonitriles in benzonitrile over HZSM-5 at various temperatures and contact times gives the points on the composition diagram shown in Figure 1. The three-component equilibrium of 46% ortho, 34% meta, and 20% para is achieved at 500 °C with a contact time of about 3 s. Dealkylation to benzonitrile is negligible as is disproportionation to benzonitrile and DMB's. The points are the result of separate experiments with different temperatures and contact times. Severity can be defined as some function of the reaction conditions which increases with either temperature or contact time. If the activation energies of the various isomerizations or adsorption/desorption differed significantly, experiments with the same conversion would have different selectivities. This is not observed so a single severity index seems sufficient to correlate the data.

Passing either 2,4-, 2,5-, or 3,4-DMB in benzonitrile over the same catalyst gives the points on the composition diagram shown in Figure 2. The three-component equilibrium is 46% 2,4-DMB, 38% 2,5-DMB, and 16% 3,4-DMB. None of the other three isomers were seen above the 1% level by either NMR or GC/MS. 2,6-DMB does not react under the same conditions in which the three component equilibrium of 2,4-, 3,4-, and 2,5-DMB is completely established. Neither dealkylation nor disproportionation to mono- and trimethylbenzonitriles is a significant side reaction under these conditions.

Table I. Kinetic Model for Methylbenzonitrile Isomerizations

		rel rate constant
Toluonitrile		
o → m		1.00
m → o		1.3
o → p		0.1
p → o		0.23
m → p		1.3
p → m		3.0
Dimethylbenzonitriles		
2,4 → 2,5		1.00
2,5 → 2,4		1.2
2,4 → 3,4		0.8
3,4 → 2,4		2.3
2,5 → 3,4		1.2
3,4 → 2,5		2.8

Other acid zeolites such as HY, H-Mordenite, and H-Omega do not catalyze these isomerizations. This result is not due to rapid coking. No reaction is observed even at very short exposure, and the unreactive catalysts remain light in color even after exposure to the nitriles.

Kinetic Model

The relative rates of the three species interconversions were determined by fitting the observed compositions to a kinetic model. Minor variations in zeolite preparation, pretreatment, and either poisons or cocatalysts in the feeds cause large variations in the absolute isomerization rates. Relative isomerization rates of the various isomers are easier to measure and are sufficient to gain mechanistic insights.

The simplest model which might be expected to fit the data includes only reactions 1 and 2. However, no combination of relative rate constants in these equations gives an acceptable fit to the data.

$$\text{ortho} = \text{meta} \quad (1)$$

$$\text{meta} = \text{para} \quad (2)$$

$$\text{ortho} = \text{para} \quad (3)$$

The simplest model which fits the data includes reaction 3.

If we assume $k_1 = 1.00$, then k_{-1} is fixed by the measured equilibrium constant. If the forward rates of eq 2 and 3 are taken as independent variables, then the reverse reactions of these equations are also constrained by the equilibrium. The problem then is to find the best values of k_2 and k_3 to fit the observed data. For each set of k 's, the six equations were integrated to equilibrium.⁶ The error of each observation in the triangular coordinate system was taken as the distance between the experimental composition and the closest point on the calculated line.

(1) Chemical and Engineering News, 12/22/80, 32.
 (2) Haag, W. O.; Olson, O. H.; Weisz, P. B. In *Chemistry for the Future*; Grunewald, H., Ed.; Pergamon: New York, 1984; p 327.
 (3) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* 1962, 27, 3464.
 (4) Keim, K. H.; Kiauk, R.; Meisenburg, E. Br. Pat. Appl. 2 012 271, 1979; *Chem. Abstr.* 92, 180815.
 (5) Arpe, H. J.; Litterer, H. Eur. Pat. Appl. Ep 92 103, 1983; *Chem. Abstr.* 100, 6057.

(6) Stabler, R. N.; Chesnick, J. *Int. J. Chem. Kinet.* 1978, 10, 461-469.

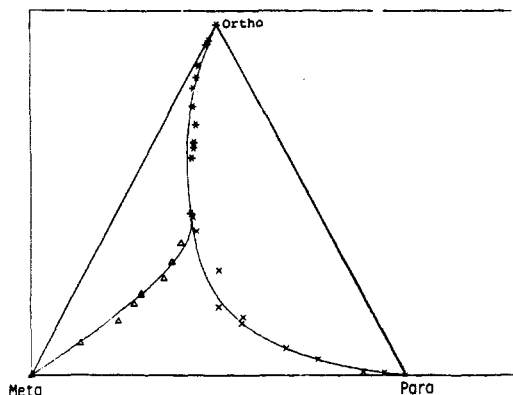


Figure 1. Composition diagram for toluonitrile isomerization.

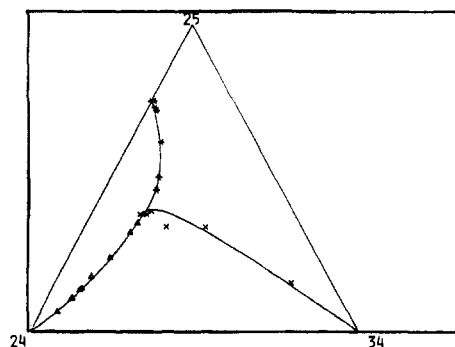


Figure 2. Composition diagram for dimethylbenzonitrile isomerization.

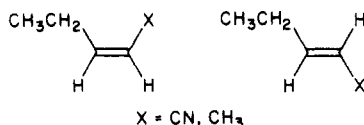
The sum of these deviations was minimized in a least-squares sense to give the relative rate constants in Table I. Points close to equilibrium were excluded from the fitting process because they had already been used to determine the equilibrium constants and thus the three reverse rates.

A similar process was used to generate the DMB rate constants. The lines in Figures 1 and 2 are the paths to equilibrium calculated by using the relative rate constants in Table I.

Discussion

Equilibrations such as these give relative free energies of isomers with an accuracy which cannot be matched by combustion analyses of each separate compound. For the DMB's, nothing can be said about the thermodynamics of the three isomers which are not substrates of this catalyst.

The toluonitrile equilibrium favors the ortho isomer. Steric effects are generally invoked to explain the relative instability of the ortho isomers.³ Conversely, there must be an attractive interaction between the cyano and the methyl substituents. A similar effect is seen in the isomer preferences of pentenenitriles. While the ratio of *cis*-/*trans*-2-hexene is 0.59 at 25 °C,⁷ the corresponding ratios of *cis*-/*trans*-2-pentenitrile is 0.83 at 25 °C.⁸



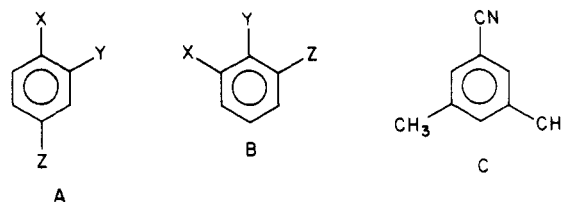
The specificity of the DMB isomerization is remarkable. The three substrate isomers all have the 1,2,4-trisubsti-

Table II. Minimum Diameters^a of Methylbenzonitriles

subst	diameter
Toluonitriles	
o	6.55
m	6.55
p	5.98
Dimethylbenzonitriles	
2,3	6.79
2,4	6.55
2,5	6.55
2,6	7.14
3,4	6.55
3,5	7.44

^a In Å.

tuted substitution pattern A. The three nonsubstrates, 2,3-, 2,6-, and 3,5-DMB, have 1,2,3- (B) and 1,3,5-trisubstituted benzene (C) structures.

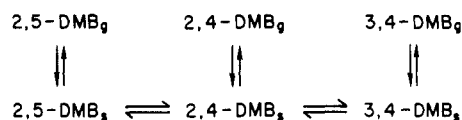


The calculated smallest possible diameters of these six isomers⁹ are given in Table II. The three substrates are all smaller than any of the three nonsubstrates. That isomers of structure A interconvert without forming either B or C is an example of product selectivity. Presumably, even if B and C could form inside the zeolite, they would be too big to diffuse out. That 2,6-DMB does not react is an example of reactant selectivity.

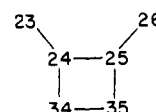
Although the relative rates of toluonitrile isomerization closely match those expected of a strictly 1,2-methyl shift, i.e., $k_{op} \ll k_{mp} \sim k_{om}$, the same is not true for the DMB isomerizations. The apparent direct interconversions of the 2,5- and 3,4-isomers have similar rate constants to those observed for the other two processes which can be written as simple 1,2-shifts.

Two slightly more complex mechanisms can account for this observation.

Gas-phase DMB's, which are the only species actually observed, are in equilibrium with surface adsorbed species. This adsorption equilibrium may not be rapid compared to surface-catalyzed isomerization reactions. Thus, a newly formed 2,4 surface species could either desorb to give gas-phase 2,4-DMB or isomerize to give either surface 2,5- or 3,4-DMB.



Alternatively, the graph of 1,2-methyl shifts in a set of dimethyl aromatics is



A direct interconversion between 3,4-DMB and 2,5-DMB is not possible. However, 3,5-DMB could form inside the zeolite by a 1,2-methyl shift and be incapable of getting

(7) Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie: Pittsburgh, 1953.

(8) McKinney, R. J., private communication.

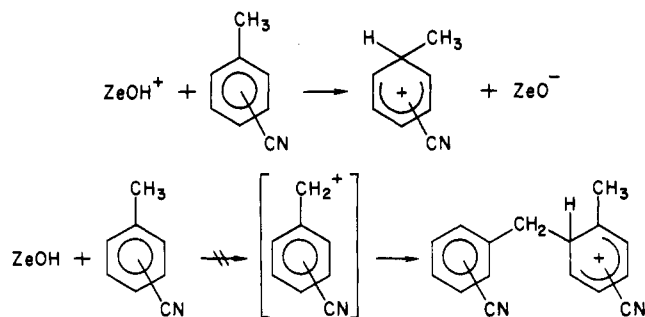
(9) Hoogenstraaten, W.; Tipker, J. *Medicinal Chemistry*; Academic: New York, 1976; Vol. II-VII, p 163.

out. The apparent direct interconversion could involve 3,5-DMB which never desorbs to be observed in the gas phase. In principle, these two alternatives could be distinguished by labeling one of the two methyl groups and observing the label in the products at very low conversions.

While CN migration is unlikely, the possibility cannot be excluded without labeling studies in the toluonitriles. Isomerizations of DMB's require methyl migrations.

Large port zeolites such as faujasites transalkylate xylenes to toluene and trimethylbenzenes.¹⁰ Smaller zeolites such as HZSM-5 and mordenite are more selective and are useful to disproportionate toluene to *p*-xylene and benzene.¹¹ HZSM-5 has shape selective sites which preclude the formation of the branched diphenylmethane intermediates proposed for the intermolecular exchange process.² That the products are formed in this reaction by intramolecular 1,2-shifts rather than an intermolecular, electrophilic mechanism is an example of transition-state selectivity.

The acid sites of HZSM-5 are unusually strong.¹¹ Thus even though large zeolites such as Y and Omega can accommodate all the substrates and transition states, they are not effective catalysts because the acid sites are not strong enough to form the intermediate carbenium ions from the deactivated methylbenzonitriles.



Experimental Section

3,4-Dimethylbenzoic acid was converted to 3,4-DMB by treatment with chlorosulfonyl isocyanate.^{12,13} The sample of 2,5-DMB obtained from Pfaltz and Bauer had some 2,4-isomer as an impurity. All other nitriles were obtained from commercial sources and used without additional purification. The GC analyses were done by using a FI detector and a 12 ft \times 1/8 in. column of 2% UCON 40 HB 5100 1% KOH on CWHP 80-100 at 120 °C. The elution order for the toluonitriles was ortho < meta < para and for the dimethylbenzonitriles 2,5 < 2,4 < 3,4.

Registry No. *o*-Toluonitrile, 529-19-1; *m*-toluonitrile, 620-22-4; *p*-toluonitrile, 104-85-8; 2,4-dimethylbenzonitrile, 21789-36-6; 2,5-dimethylbenzonitrile, 13730-09-1; 3,4-dimethylbenzonitrile, 22884-95-3.

(10) Lanewalda, M. A.; Bolton, A. P. *J. Org. Chem.* 1969, 34, 3107.

(11) Wang, I.; Chen, T. J.; Chaa, K. J.; Tsai, T. C. *J. Catal.* 1979, 60, 140.

(12) Lohaus, G. *Org. Synth.* 1970, 50, 18.

(13) Friedman, L.; Shechter, H. *J. Org. Chem.* 1961, 26, 2522.

Directing Effects in Homogeneous Hydrogenation with [Ir(cod)(PCy₃)(py)]PF₆

Robert H. Crabtree* and Mark W. Davis

Chemistry Department, Yale University, New Haven, Connecticut 06511

Received February 20, 1986

The presence of a ligating group, e.g., OH, CO₂Me, C=O, or OMe, on an olefinic substrate is shown to direct the attack of the hydrogenation catalyst [Ir(cod)(PCy₃)(C₆H₅N)]PF₆/H₂/CH₂Cl₂ from the face of the molecule containing the directing group. Isomerization is a minor side reaction in the cases studied. The origin of this effect is discussed and a model intermediate isolated.

One of the important advantages of homogenous over heterogeneous catalysis is selectivity. This has been strikingly shown by the achievement of both stereo- and enantioselective control in a number of organic transformations, of which the Sharpless¹ asymmetric epoxidation is perhaps the most significant. We report here on the way that a ligating group, particularly OH, in certain olefinic substrates can bind the catalyst and so direct addition of H₂ from that face of the molecule which contains the ligating group. This has only been reported for a restricted range of catalysts, including our own [Ir(cod)(PCy₃)(py)]PF₆, which are sufficiently coordinatively unsaturated in their active form to be able to bind the ligating group as well as H₂ and the C=C double bond. Heterogeneous catalysts have also been known to show directing effects, but these are much less strong and much less predictable than those described here.²

The first observation of a directing effect in homogeneous hydrogenation was reported by Thompson,³ who showed, as early as 1974, that directed reduction of a tricyclic homoallylic alcohol, stigmasterol, was possible using the lithium salt of the alcohol with RhCl(PPh₃)₃ as catalyst. In 1982, Brown and Naik^{4a} described the reduction of various unmodified acyclic chiral allylic and homoallylic alcohols with [(nbd)Rh(dppb)]PF₄ (dppb = PPh₂P(CH₂)₄PPh₂) in CH₂Cl₂ to give product diastereomer ratios as high as 97:3.

Prompted by the work of Brown and Naik, we,⁵ Evans and Morrissey,⁶ and Stork and Kahne⁷ have recently

(3) Thompson, H. W.; McPherson, E. *J. Am. Chem. Soc.* 1974, 96, 6232.

(4) (a) Brown, J. M.; Naik, R. G. *J. Chem. Soc., Chem. Commun.* 1982, 348. (b) Brown, J. M.; Hall, S. A. *Tetrahedron Lett.* 1981, 25, 1393; (c) *J. Organomet. Chem.* 1985, 285, 333.

(5) Crabtree, R. H.; Davis, M. W. *Organometallics* 1983, 2, 681.

(6) Evans, D. A.; Morrissey, M. M. *Tetrahedron Lett.* 1984, 25, 4637; *J. Am. Chem. Soc.* 1984, 106, 3866.

(7) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* 1983, 105, 1072.

(1) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* 1980, 102, 5974.
(2) Thompson, H. W.; Naipawer, R. E. *J. Am. Chem. Soc.* 1973, 95, 6379 and references therein.