3-(Diethylamino)-2,4-dimethyl-4-vinyl-2-cyclobuten-1-one (27): 0.62 g, 3.21 mmol, 35.4%; oil; IR (film) 1750, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, Me, $J_{CH_2CH_3}$ = 7.8 Hz), 1.27 (t, 3 H, Me, $J_{CH_2CH_3}$ = 7.8 Hz), 1.43 (s, 3 H, Me), 1.73 (s, 3 H, Me), 3.36 (q, 2 H, CH_2), 3.44 (q, 2 H, CH_2), 5.0–5.33 (m, 2 H of H_2C=CH), 5.78–6.17 (m, 1 H of H_2C=C*H*); ^{13}C NMR ($CDCl_3$) δ 7.09 (2 Me), 13.75 (Me), 16.92 (Me), 42.68 (CH_2), 44.47 (CH_2), 64.03 (C), 105.84 (C), 115.48 (CH_2), 139.08 (CH), 170.78 (C), 187.70 (C); mass spectrum, *m/e* 193 (M^+), 178, 121, 111, 82. Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.69; H, 9.96; N, 7.21.

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HZSM-5-Catalyzed Isomerization of Alkylanilines†

F. J. Weigert

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

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Zeolite HZSM-5 catalyzes the equilibration of toluidines and ethylanilines by an intramolecular 1,2-shift mechanism. The three xylidines with the 1,2,4-substitution pattern are also interconverted by this catalyst. Larger methylanilines are neither formed nor consumed by the catalyst.

HZSM-5 has been a popular catalyst for the isomerization of substituted toluenes.[1] It has extremely strong acid sites, and its intermediate-size pores resist coke formation better than the larger pore faujasites. The three-dimensional pore structure is less resistant to blockage than the one-dimensional pore structure of mordenites. Industrial processes using solid acids cause much less corrosion than processing using more traditional Lewis acids such as $AlCl_3$. Xylene equilibration using HZSM-5 is practiced on a large scale to prepare the para isomer as a polyester intermediate.[2]

Though less important commercially, reports on the isomerization of other substituted toluenes with HZSM-5, such as chlorotoluenes,[3] cresols,[4] and toluonitriles,[5] have appeared; but at the time this work was begun, toluidine isomerization had not been reported. Patents describing work overlapping ours[6] have appeared.[7]

Under more severe conditions, HZSM-5 has been reported to isomerize aniline and phenylenediamines to methylpyridines and aminopicolines.[8,9]

We present here a study of the HZSM-5-catalyzed isomerization of alkylanilines.

Results

A mixture of each toluidine in aniline was passed over HZSM-5. We could only feed liquids to our reactor, so as to keep the reaction conditions as similar as possible, all reagents were fed in aniline as solvent. The toluidine isomer profile from pure *o*-toluidine as the starting material was the same as for the solution of *o*-toluidine in aniline. Dealkylation and transalkylation do not occur except under the most severe conditions. No methylpyridine was detected in these experiments, which were run under conditions much milder than previous work.[8,9]

Table I. Equilibrium Compositions for Alkylanilines

	o	*m*	*p*
xylenes[a]	23	53	24
toluidines	31	52	17
ethylanilines	24	57	19
dimethylanilines[b]	23	26	51

[a] Reference 12, 600 K. [b] Orientations of methyls: 3,4; 2,4; 2,5.

The toluidine isomer distribution of the reaction products is shown in Figure 1 as a composition diagram. Each vertex represents a pure isomer, each edge a binary mixture, and a point inside represents a ternary mixture. There is one unique equilibrium point in the interior of such a triangle. The advantages of such a coordinate system have been described previously.[10]

Each symbol represents a separate experiment in which the independent variables were contact time, partial pressure, aniline/toluidine ratio, and temperature. A single variable, severity, suffices to explain the progress of the reaction as can be seen by the narrow band of the data points from each starting isomer. A similar plot for the ethylanilines is given in Figure 2. The equilibria deter-

† Contribution 4216.

(1) Haag, W. O.; Olson, O. H.; Weisz, P. B. In *Chemistry for the Future*; Grunewald, H., Ed.; Pergamon: New York, 1984; p 327.
(2) *Chem. Eng. News* **1980**, *58* (Dec 22), 32.
(3) (Toray Industries) Japan Kokai Tokkyo Koho JP 82 85 330 1982; *Chem. Abstr.* **1982**, *97*, 197966. Baltes, H.; Leupold, E. I. (Hoechst A. G.) Ger. Offen. DE 3 334 674, 1985; *Chem. Abstr.* **1985**, *103*, 160201.
(4) Keim, K. H.; Kiauk, R.; Weisenburg, R. Br. Pat. Appl. 2 012 271, 1979; *Chem. Abstr.* **1980**, *92*, 180815.
(5) Weigert, F. J. *J. Org. Chem.* **1986**, *51*, 2653.
(6) Weigert, F. J. U.S. Patent 4 593 124, 1986.
(7) Arpe, H. J.; Litterer H. (Hoechst) Eur. Pat. 92 103, 1982; U.S. Patent 4 480 128, 1984. Eichler, K., Leupold, E., Arpe, H. J., Baltes, H. Ger. Offen. DE 3 420 707, 1985; Chem. Abstr. **1986**, *104*, 129608.
(8) Chang, C. D., Perkins, P. D. *Eur. Pat. Appl.* EP 82 613, 1983; *Chem. Abstr.* **1983**, *99*, 139788.
(9) LeBlanc, H.; Puppe, L. Ger. Offen. DE 3 332 687, 1985; *Chem. Abstr.* **1985**, *103*, 6239.
(10) Weigert, F. J. *J. Catal.* **1987**, *103*, 20.

0022-3263/87/1952-3296$01.50/0

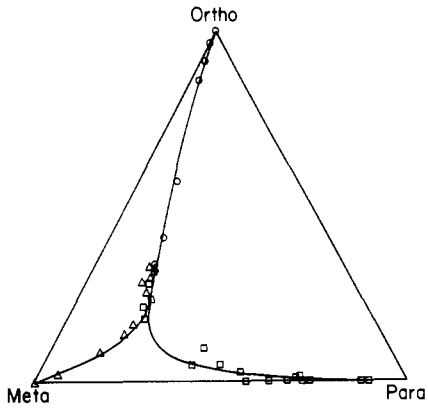

Figure 1. Composition diagram for toluidine equilibration with HZSM-5.

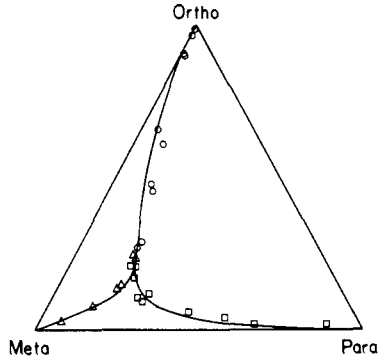

Figure 2. Composition diagram for ethylaniline equilibration with HZSM-5.

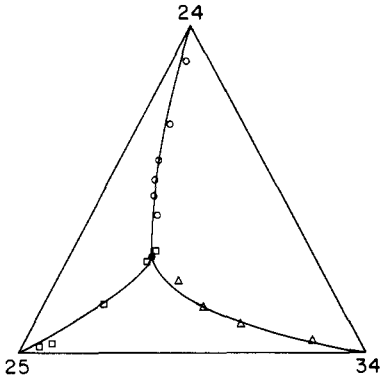

Figure 3. Composition diagram for dimethylaniline equilibration with HZSM-5.

mined for the toluidines and ethylanilines are given in Table I.

Mixtures of each of the six dimethylanilines (DMAs) in aniline were also passed over HZSM-5. Only three of the isomers reacted, 2,4, 2,5, and 3,4. These three interconverted as shown by the composition diagram in Figure 3. The other three isomers neither reacted nor were formed from any of the three reactive isomers.[9] Also, to confirm the intramolecular nature of this reaction, only traces of toluidines were formed, and these only under the most severe conditions where dealkylation is the probable reaction. The three-component DMA equilibrium is also given in Table I. Isopropylanilines dealkylate under similar conditions.

The simplest mechanism to explain the product compositions of the alkylaniline isomerizations is a series of reversible 1,2-methyl shifts (eq 1).

$$\text{ortho} \underset{k_{-1}}{\overset{k_1}{=}} \text{meta} \underset{k_{-2}}{\overset{k_2}{=}} \text{para} \qquad (1)$$

Table II. Relative Rate Constants for Alkylaniline Isomerization of HZSM-5

	om	*mo*	*mp*	*pm*	*po*	*op*
toluidines	=1.00	0.6	2.0	6.1	0.0	0.0
ethylanilines	=1.00	0.4	0.9	2.7	0.0	0.0
dimethylanilines[a]	=1.00	0.9	1.5	0.8	1.6	3.6

[a] *o*, *m*, and *p* refer to methyl orientation, i.e.: 3,4 = *o*; 2,4 = *m*; 2,5 = *p*.

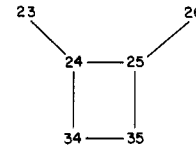

Figure 4. 1,2-Intramolecular shift graph for DMA interconversion.

The four unknown rate constants required in this model can be reduced to three if only relative rates are considered. Equilibrium considerations fix two more parameters, leaving only one independent variable. The differential equations were integrated to equilibrium with several values for the independent variable and the deviation between the calculated path and the observed compositions in triangular space summed for all observations.[11] The lines shown in Figures 1 and 2 are the best fits in a least-squares sense. The rate constants are given in Table II. The fits were not improved by adding the two additional equations for the direct interconversion of the ortho and para isomers.

A similar procedure was used to model the DMA exchange. Although a rigorous 1,2-shift mechanism would preclude a direct interconversion of the 2,5- and 3,4-isomers, the best fit to the observed data required a significant value for this rate constant.

Discussion

The thermodynamics of the toluidine systems is very similar to that of the xylenes[12] and quite unlike that of the halotoluenes.[13] The similarity of the thermodynamics of the methyl and ethylanilines suggests that the CH_3 of the ethyl group does not interact with the NH_2 in the ortho isomer. The three DMAs have very similar free energies as would be expected based on pairwise additivity considerations of xylenes and toluidines.

The same alkylaniline composition has been achieved by starting from all three vertices of the composition triangle. This composition still may not be the actual equilibrium if the rate of decomposition of one of the species to other products is very different from that of the other two. On the other hand, computer simulations have shown that even if the rate of decomposition of all three products is large relative to the rate of their mutual interconversion, the convergence point does represent equilibrium.

In this case the leakage rate is less than 10% of the equilibration rates and there is no evidence that any one of the isomers is dealkylated faster than any other. Thus we believe that the convergence points in Figures 1–3

(11) Theoretical kinetic analyses were performed by the Gear integration program HAVCHEM[17] modified for use within our PDP-10 and VAX time-sharing environment. Weigert, F. J. *Comput. Chem.* in press.
(12) Stull, D. R.; Westrum, D. R., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.
(13) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1962**, *27*, 3464.

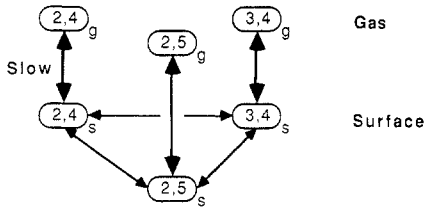

Figure 5. Dimethylaniline equilibration mechanism involving slow desorption of surface 2,4-DMA.

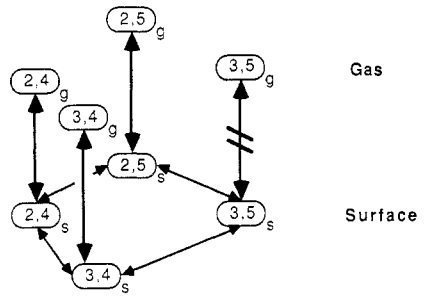

Figure 6. Dimethylaniline equilibration mechanism involving surface 3,5-DMA.

represent a true equilibrium.

The relative rate constants for toluidine and ethylaniline isomerization are consistent with a pure 1,2-shift mechanism. The apparent direct interconversion of 3,4- and 2,5-DMA requires further consideration. The interconversion network of the six DMA's involving only 1,2-shifts is shown in Figure 4.

This simplified model assumes that surface and gas-phase species are in rapid equilibrium. The apparent direct interconversion of 2,5 and 3,4 could be the result of slow desorption of either 2,4- or 3,5-DMA from a catalyst site.

The observed kinetics could be explained by assuming slow desorption of 2,4-DMA relative to the surface equilibration reactions as shown in Figure 5. Since our analytical procedure only detects gas-phase species, the apparent result is a direct path from 2,5-DMA to 3,4-DMA without passing through gas-phase 2,4-DMA.

The three DMA's that do not have a 1,2,4-substituent pattern may form inside the zeolite pore structure but not desorb. A surface equilibrium of all six surface species could be established as shown for the central four species in Figure 6, but only the three smallest isomers could desorb to the gas phase to be detected. Surface 3,5-DMA or 2,4-DMA could both be unobserved intermediates between gas-phase 2,5-DMA and 3,4-DMA.

The two possibilities of 2,4- or 3,5-DMA as the surface intermediate could in principle be distinguished by labeling one of the methyls of 2,4-DMA and observing the distribution in the other at very low conversions. The symmetry plane of any 3,5-DMA formed would scramble to the label; the label would remain distinct if the intermediate were the 2,4-isomer.

Table III. Diameters of Alkylanilines

subst	*o*	*m*	*p*
Me	6.52	6.52	5.98
Et	6.52	6.52	5.98
Me_2[a,b]	6.55	6.55	6.52

[a] Orientation is that of Me groups. [b] Diameters of the other isomers are: 2,6-DMA = 2,3-DMA = 6.78; 3,5-DMA = 7.38.

The minimum diameters of these compounds are given in Table III.[14] An effective pore size of between 6.55 and 6.78 Å can be estimated for HZSM-5 from these studies. The cutoff is quite sharp.

DMA isomerization demonstrates three separate types of zeolite selectivity: starting material, product, and transition state.[15] Starting material selectivity is shown because only three smallest DMA's react. Product selectivity is shown because the three largest DMA's do not form. Transition-state selectivity is shown because the mechanism involves intramolecular 1,2-methyl shifts rather than an intermolecular transalkylation.[16]

Conclusion

Conventional synthesis of alkylanilines generally involves electrophilic nitration of the appropriate alkylbenzene followed by reduction. *m*-Toluidine is available only in limited quantities by this technology as the major toluene nitration products are the ortho and para isomers. This chemistry provides a means of producing the *m*-toluidine from the more readily available *o*- and *p*-toluidine.

Experimental Section

Solutions of alkylanilines in aniline were passed over HZSM-5 catalyst contained in a Vycor reactor heated in a split-tube furnace. Nitrogen was used as a carrier gas and to adjust the partial pressure of the reactants.

Typical conditions are as follows: liquid flow rate, 2 mL/h; N_2, 5 mL/min; 5 g of zeolite; temperatures between 250 and 450 °C. For each set of conditions, the system was allowed to stabilize for about 0.5 h, and then a liquid sample was collected for a few minutes.

The products were analyzed by gas chromtography on a 50M Carbowax capillary column with a flame ionization detector at 200 °C. Preliminary work used a 12 ft × $^1/_8$ in. column of 2% UCON 40 HB 5100 1% KOH on CWHP 80-100 at 150 °C and a thermal conductivity detector.

(14) Hoogenstraaten, W.; Tipker, J. *Medicinal Chemistry*; Academic: New York, 1976; Vol. II–VII, pp 163–207.
(15) Derouane, E. G.; Dejaifve, P.; Gabelica, Z.; Vedrine, J. C. *Faraday Discuss. Chem. Soc.* **1982**, *72*, 331.
(16) Weigert, F. J.; Mitchell, R. S., unpublished work.
(17) Stabler, R. N.; Chesnick, J. *Int. J. Chem. Kinet.* **1978**, *10*, 461.