ard conditions there was obtained, after numerous extractions with Claisen alkali, a small amount of liquid, $n^{20}\text{D}$ 1.5808. Since the refractive index was not altered by heating the compound at 200° for several hours this was assumed to be C-alkylation product. No further study of the substance was made.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE PITTSBURGH CONSOLIDATION COAL COMPANY, RESEARCH AND DEVELOPMENT DIVISION]

Silica–Alumina Catalyzed Isomerization–Disproportionation of Cresols and Xylenols

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Vapor phase isomerization–disproportionation of the isomeric cresols and xylenols in the presence of synthetic silica–alumina catalyst is described. At a maximum conversion temperature of 344° silica–alumina shows a very high selectivity for isomerization–disproportionation of methyl groups in alkyl phenols. The detailed product distribution was determined with varying depths of conversion. From the nature of the primary isomerization products, evidence is presented for the stepwise shift of methyl groups. The effect of steric hindrance on the isomerization and disproportionation reactions is discussed.

The aluminum chloride-catalyzed isomerization of *p*-cresol to *m*-cresol was first reported by Norris and Turner.[1] Baddely[2] described the $AlCl_3$ catalyzed isomerization of *o*-, *m*- and *p*-cresol and a number of individual xylenols at temperatures from 125–135°. Quantitative data were presented on the rate of isomerization of *p*-cresol. Since a minimum of one mole of aluminum chloride was used per mole of alkyl phenol, the actual compounds studied were aryloxy aluminum chlorides. Baddely concluded that *o*-cresol does not isomerize or form from the isomerization of *m*- or *p*-cresol. Meissner and French[3] re-examined the aluminum chloride-catalyzed isomerization–disproportionation of the isomeric cresols. They found that all three cresols isomerize using a molar excess of aluminum chloride and suggested that Baddely's conclusions regarding *o*-cresol were based on inadequate analytical procedures.

Aluminum fluoride was used by Nickels[4] for vapor phase isomerization–disproportionation of *o*-cresol. Given[5] described the vapor phase isomerization–disproportionation of cresols and xylenols over silica–alumina type catalysts using relatively large quantities of steam as a diluent at temperatures from 360–400°. Detailed product distribution was not presented.

Our investigation covers vapor phase silica–alumina catalyzed isomerization–disproportionation of the individual isomeric cresols and xylenols at lower temperatures. Complete product distribution will be presented as determined by infrared absorption analysis. An attempt will be made to account for the variations in product distribution with depth of conversion in terms of a mechanistic picture of methyl group migration.

Experimental

The pure compounds, except *p*-cresol, were purchased from Reilly Tar and Chemical Co. in a purity of 90–98%. Synthetic *p*-cresol was obtained from Hercules Powder Co. The compounds were further purified by precise fractionation, a heart cut being retained in each case.

The catalyst was synthetic silica–alumina Grade 111 obtained from Davison Chemical Co. The average analysis is 88% silica and 12% alumina. The average surface area is 372 m.^{2}/g.

The experimental apparatus was similar in design to the apparatus previously described[6] for thermal cracking of alkyl phenols. It consisted of a precision liquid feeder, stainless steel reactor 1″ × 36″, and a product recovery system. Nitrogen gas was used as an inert diluent.

Fresh catalyst was used for each experiment. A 30-minute lineout period was employed at the beginning of each run. The condensed liquid product was transferred with benzene. The benzene solution was dried azeotropically and distilled into seven alkyl phenol cuts on a precision fractionation column. The cuts were analyzed for phenol, *o*-, *m*-, *p*-cresol, the six isomeric xylenols, 2,4,6- and 2,3,6-trimethylphenol using a modification of the infrared method of Friedel.[7]

Analyses were made on a Baird double beam spectrophotometer using NaCl optics. The remaining C_9-phenols boiling above 3,4-xylenol were determined as a group by distillation using acenaphthene as a backing liquid. The fraction of the products boiling above acenaphthene was reported as residue. Carbon was determined by difference. The gas was analyzed by a gravimetric method described by Barthauer, *et al.*[8]

Discussion of Results

The results of the conversion of the three isomeric cresols at 344° are shown in Table I. One striking fact is the greater lability of the methyl group in the cresols as compared with the corresponding xylenes.[9] Temperatures in excess of 450° would be required to obtain the same conversion of xylenes at an equivalent space rate. The amount of isomerization varied from 29.0 to 39.4% of the converted

TABLE I

CONVERSION OF THE ISOMERIC CRESOLS

Experimental Conditions: temperature, 344°; partial pressure of alkyl phenol, 0.4 atm.; vapor minute space velocity (VMSV), 7.0 min.$^{-1}$; liquid hourly space velocity (LHSV), 0.4 hr.$^{-1}$.

Starting isomer	*o*-Cresol	*m*-Cresol	*p*-Cresol
Conversion, wt. %	50	43	87
Compn. of converted products, wt. %			
Phenol	27.8	17.3	20.4
Cresols (isom.)	29.0	35.2	39.4
Xylenols (disprop.)	28.7	17.2	21.9
Neutrals	0.5	2.5	0.5
Residue	4.9	21.4	14.0
Carbon	8.7	6.4	3.4
Gas	0.1	. .	. .

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[1] J. F. Norris and H. S. Turner, THIS JOURNAL, **61**, 2128 (1939).

[2] G. Baddely, *J. Chem. Soc.*, 525 (1943).

[3] H. P. Meissner and F. E. French, THIS JOURNAL, **74**, 1000 (1952).

[4] J. E. Nickels, U. S. Patent 2,551,628 (May, 1951).

[5] P. H. Given, British Patent 695,464 (August, 1953).

[6] B. W. Jones and M. B. Neuworth, *Ind. Eng. Chem.*, **44**, 2872 (1952).

[7] R. A. Friedel, *et al.*, *Anal. Chem.*, **22**, 418 (1950).

[8] G. L. Barthauer, *et al.*, *ibid.*, **25**, 256 (1953).

[9] P. H. Given and D. L. Hammick, *J. Chem. Soc.*, 1779 (1949).

product. The disproportionation products, phenol and xylenols, make up most of the remaining product starting with *o*- or *p*-cresol. In the case of *m*-cresol, non-distillable residue amounts to 21% of the converted feed.

To obtain a better understanding of the primary processes involved in isomerization of cresols, the conversion temperature was reduced. The data for *o*-cresol at 288° are summarized in Table II. Three experiments were performed in which the vapor space rate was varied from 1.4 to 10.8 (min.$^{-1}$), all other variables being held constant. The decrease in vapor space rate is reflected in a decrease in conversion from 40.2 to 6.8%. Of particular importance is the increase in *m*-cresol concentration in the isomerized cresols from a *m*–*p*-cresol ratio of 2.5 to 13.6 at the shortest vapor contact. This latter ratio corresponds to a concentration of 93.0% *m*-cresol in the isomerization products.

TABLE II

CONVERSION OF *o*-CRESOL

Conditions		288°	
VMSV, min.$^{-1}$	1.4	5.5	10.8
LHSV, hr.$^{-1}$	0.18	0.75	1.47
Partial pressure, atm.	0.93	0.97	0.97
Conversion, wt. %	40.2	19.3	6.8
Distribution of converted products, wt. %			
Phenol	31.5	28.5	9.8
Cresols, *m*	17.5	16.9	23.0
p	7.2	4.8	1.7
Xylenols	26.9	16.2	17.4
C_9-Phenols	6.2	2.5	0.5
Residue	4.2	8.5	19.6
Gas	...	...	...
Carbon	6.2	22.1	28.7
m-/*p*-Cresol ratio	2.5	3.5	13.6

These data indicate that *m*-cresol is the primary isomerization product. The isomerization of methyl groups can be considered a stepwise process, the methyl group moving to adjacent aromatic carbons in steps. The first step in the isomerization process involves reaction of *o*-cresol with a proton from the silica–alumina catalyst forming a proton–alkyl phenol complex. The second step is a shifting of a methyl group to a position where it is shared by the adjacent aromatic carbon. The third step is a rearrangement to the adjacent carbon and dissociation to *m*-cresol and a proton. *p*-Cresol is formed in an analogous manner by repetition of the previous step. A similar mechanism was postulated by McCaulay and Lien[10] to account for the liquid phase isomerization products from methylbenzenes catalyzed by hydrogen fluoride–boron fluoride mixtures.

The applicability of this isomerization mechanism to the individual xylenols was explored. Of the individual xylenols, 2,6-xylenol is the only isomer which would have a single primary isomerization product resulting from the stepwise shift of one methyl group to the adjacent 3- or 5-position. The shift of either methyl group would produce 2,5-xylenol as the primary isomerization product. The conversion of 2,6-xylenol was explored over a range of vapor space rates from 1.18 to 23.7 (min.$^{-1}$). The data at 288° are shown in Table III. The conversion of 2,6-xylenol is almost exactly twice that of *o*-cresol at the same conditions. The concentration of 2,5-xylenol increases from 31.6% of the isomerization products at the longest vapor contact time to 61.4% at the shortest vapor contact. This would indicate that 2,5-xylenol is the primary isomerization product in agreement with a stepwise isomerization of the methyl group.

TABLE III

CONVERSION OF 2,6-XYLENOL

Conditions		288°		
VMSV, min.$^{-1}$	1.2	6.0	12.0	24.0
LHSV, hr.$^{-1}$	0.17	0.35	0.72	1.43
Partial pressure, atm.	0.92	0.37	0.36	0.38
Conversion, wt. %	81.4	59.0	39.9	27.9
Distribution of isomerization products, %				
2,3	5.9	6.1	9.2	12.7
2,4	37.7	23.5	16.5	15.5
2,5	31.6	49.5	58.7	61.4
3,4	13.9	9.1	7.6	2.8
3,5	10.9	11.8	8.0	7.6

Catalytic conversion of a number of other xylenol isomers was studied. The predicted primary products based on either methyl group moving to an adjacent aromatic carbon atom are shown under the appropriate starting xylenol. The isomerization products observed experimentally for the conversion of 2,4-xylenol, 2,5-xylenol, 3,5-xylenol and 3,4-xylenol at 288° are included. As a reference point, the equilibrium xylenol isomer distribution is approximately

Equilibrium distribution of xylenols, %

2,3-Xylenol	9.0	2,6-Xylenol	11.0
2,4-Xylenol	30.0	3,4-Xylenol	12.0
2,5-Xylenol	24.0	3,5-Xylenol	14.0

This distribution was estimated from the observed isomer distribution resulting from conversion of 3.4-xylenol and 2,4-xylenol at 344°. The conversions were 88 and 95%, respectively.

In the case of 2,4-xylenol, three primary products are possible. Of the three, 2,5-xylenol is the major isomer, occurring in a concentration of 58.9% of the isomerization products. Starting with 2,5-xylenol, three primary products are possible. Of the predicted isomers, 2,4-xylenol is the major isomer. The low yield of 2,6- and 3,5-xylenol can be attributed to their relatively low equilibrium concentrations. The predicted primary products from 3,5-xylenol are 2,5- and 3,4-xylenol. The latter isomers comprise 83% of the isomerization products. Starting with 3,4-xylenol, 3,5- and 2,4-xylenol are the predicted primary products. These isomers are observed in a concentration of 73% of the isomerization products.

Examination of the composition of the isomerization products from various xylenols shows in all cases the primary isomerization products are the isomers predicted by shifting of a methyl group to an adjacent carbon. However, many of the predicted primary products are present in low concentrations. This would indicate that there is a preferred path for primary shifting of the methyl groups. The predicted primary products which involve shifting of a methyl group into a vicinal position are underlined. Movement of a methyl group into a vicinal position involves steric hindrance with either an adjacent methyl group or hydroxyl group. This would not be a preferred path.

In the case of isomerization of 2,4-xylenol, the preferred primary product involving non-vicinal isomerization is obtained. Starting with 2,5-xylenol, 3,5-xylenol a preferred isomer from steric considerations is found in a relatively low concentration. Electrical factors play a role in determining the path of isomerization in addition to steric factors. In the case of 3,4-xylenol, the major primary product is 3,5-xylenol. This relatively high concentration of 3,5-xylenol as compared with the predicted equilibrium value provides an experimental basis for the role of steric hindrance in determining the primary isomerization products.

The stepwise isomerization mechanism coupled with the effect of steric hindrance explains the isomerization results with cresols and xylenols satisfactorily. A similar mechanism should apply to disproportionation involving bimolecular attack of an alkyl phenol–proton complex on a second alkyl phenol molecule. McCaulay and Lien[11] have suggested such a mechanism to explain the disproportionation of alkyl benzenes catalyzed by BF_3—HF mixtures. This type of process would involve a bimolecular complex in which a methyl group is shared between two alkyl phenol molecules. This is followed by transfer of the methyl group resulting in disproportionation. This type of mechanism precludes even the transitory existence of a free methylcarbonium ion.

Similar mechanisms have been proposed to explain the acid-catalyzed alkylation of phenols with olefins. Alkylation occurs *ortho* and *para* to the hydroxyl group due to the

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(10) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

(11) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

TABLE IV

XYLENOL ISOMER DISTRIBUTION[b,c]

Experimental conditions: (1) VMSV 6.0 min.$^{-1}$. (2) VMSV 12.0 min.$^{-1}$. (3) Partial pressure, 0.37 atm. (4) Temperature 288°.

Starting isomer	2,4-Xylenol	2,5-Xylenol	3,5-Xylenol	3,4-Xylenol
Predicted primary products	**3,4** 2,5 **2,3**	2,4 **2,6** 3,5	**2,5** **3,4**	3,5 **2,4**
Exptl. compn., wt. % isomn. prod.	(1)	(2)	(1)	(2)
2,3-Xylenol	8.4	15.3	4.6	7.5
2,4-Xylenol	..	46.4	7.2	28.8
2,5-Xylenol	58.9	..	31.1	18.4
2,6-Xylenol	13.6	7.3	5.0	1.1
3,4-Xylenol	8.1	15.7	52.0	..
3,5-Xylenol	11.0	15.3	..	44.2

TABLE V

ISOMERIZATION–DISPROPORTIONATION OF VARIOUS XYLENOLS[b,c]

Starting isomer	2,4-Xylenol	2,5-Xylenol	2,6-Xylenol	3,4-Xylenol	3,5-Xylenol
Conversion, wt. %	73	60[a]	59	63	35
Distribution of converted products, wt. %					
Isomerization	27.3	53.6	37.4	33.2	42.5
Disproportn. C_9	33.0	25.8	27.4	27.0	22.8
o-Cresol	11.7	3.3	22.2	1.4	2.1
m-Cresol	8.7	16.2	6.2	25.6	12.5
p-Cresol	8.1	..	0.5	2.3	1.9

[a] Estimated from experiment at higher VMSV. [b] Temperature, 288°. [c] VMSV, 6.0 min.$^{-1}$.

electron releasing ability of the hydroxyl oxygen into these positions. The alkyl phenol–proton complex should attack the *ortho* and *para* positions. The xylenol fraction produced from disproportionation of *o*-cresol at 288° (VMSV, 10.8) contained 73% 2,4- and 2,6-xylenol.

The rate of alkylation is decreased significantly when a methyl group occurs adjacent to a position *ortho* or *para* to the hydroxyl group.[12] The presence or absence of methyl groups adjacent to the available positions for substitution should affect the relative rates of isomerization and disproportionation if the mechanism previously suggested applies. The distribution of isomerization and disproportionation products starting with a number of xylenol isomers is shown in Table V. The ratio of disproportionation and isomerization products in the case 3,4-xylenol, 2,4-xylenol and 2,6-xylenol is approximately 1.0. These isomers have an unhindered *ortho* or *para* position available for disproportionation. In the case of 2,5-xylenol, intermolecular transfer of a methyl group to the 4- or 6-position is hindered by the 5-methyl group. It has been shown earlier that isomerization proceeds by shifting of the 5-methyl to the 4-position which is unhindered. This situation results in a significantly higher yield of isomerization products, more than double the disproportionation yield. The case of 3,5-xylenol is somewhat unique. Both isomerization and disproportionation are sterically unfavorable. The net result is a significant decrease in over-all conversion to 35% as compared with values of 59 and 73% for the other isomers. The observed higher rate of isomerization as compared with disproportionation can be explained by the relative size of the methyl group as compared with a second molecule of xylenol required for disproportionation.

The compositions of the cresols resulting from the disproportionation of the various xylenols are shown for each starting xylenol in Table V. For the symmetrical xylenols-2,6 and -3,5 the predicted cresol isomer is produced as the major product accompanied by a small amount of isomerization. In the case of 2,5- and 3,4-xylenol a concurrent reaction can occur in the intermolecular transfer of a *m*-methyl group and an *o*- or *p*-methyl group, respectively. From the composition of the cresols produced, it appears that the *m*-methyl group is considerably more stable to disproportionation than either the *o*- or *p*-methyl groups. The composition of the cresols obtained from 2,4-xylenol is in accord with an equal rate of disproportionation for the *o*- and *p*-methyl groups if the effect of the relative rates of isomerization of *o*- and *p*-cresol is considered.

Isomerization and disproportionation represent the major reactions in the conversion of cresols and xylenols. In addition to these reactions a small amount of the starting compound is converted to carbon and non-distillable residue. These high molecular weight products result from deep-seated reactions due to a lack of selectivity of the catalyst. In the case of *o*-cresol (Table II), the yield of carbon and residue varied from 3.0 to 6.0% of the starting material over a range of conversions from 6.8 to 40.2%. Similarly, starting with 2,6-xylenol the yield of carbon and residue varied from 3.0 to 5.0% of the feed over a range of conversions from 27.9 to 81.4%.

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[12] D. B. Luten and A. de Benedictis, U. S. Patent 2,435,087 (January, 1948).