[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, MIDLAND DIVISION, THE DOW CHEMICAL COMPANY]

Kinetics of Three-compound Equilibrations. II. The Isomerization of Xylene[1]

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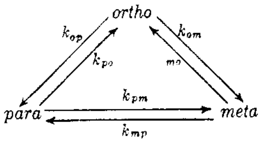
The isomerization of xylene was studied as a three-compound equilibration involving six rate constants. Dilute solutions of four xylene isomer distributions in toluene were isomerized at 50° with aluminum chloride. In each case samples were taken periodically, analyzed for *o*-xylene by vapor phase chromatography and for *m*- and *p*-xylene by differential infrared analysis. The isomer distributions obtained are consistent with the following relative rate constants and equilibrium percentages: $k_{op} = k_{po} = 0$, $k_{om} = 3.6$, $k_{mo} = 1.0$, $k_{pm} = 6.0$, $k_{mp} = 2.1$, $O^* = 17$, $M^* = 62$, $P^* = 21$. This work shows that *o*- and *p*-xylene do not directly interconvert and therefore that the isomerization of xylene proceeds by an intramolecular 1,2-shift.

Introduction

It has been shown[2] that for certain three-compound equilibrations involving six rate constants, as



the integrated rate expressions are

$$O(t) = O^* + Ae^{-\alpha\tau} + Be^{-\beta\tau} \qquad (1)$$
$$P(t) = P^* + Ce^{-\alpha\tau} + De^{-\beta\tau}$$

where $O(t)$ is the concentration of the *ortho*-isomer at time *t*, O^* is the equilibrium concentration of *ortho*- isomer, *A* and *B* are determined from the starting concentrations, α and β from the rate constant set, and τ is some function of time. The use of this scheme for the study of the isomerization of cymenes has been reported,[2] and we now have applied it to the isomerization of xylenes.

The isomerization of xylenes has been studied by Norris using $AlCl_3$,[3] by Pitzer using $AlBr_3$[4] and by Baddeley using $AlBr_3$.[5] Baddeley proposed that since the isomerization was accompanied by very little disproportionation to toluene and trimethylbenzenes, the isomerization of xylenes proceeds by an intramolecular 1,2-shift. McCaulay and Lien, using $HF \cdot BF_3$, confirmed this mechanism by showing that the isomerization of xylenes is first order in the starting xylene and that *p*-xylene isomerizes to *m*-xylene without the formation of *o*-xylene, and *o*-xylene isomerizes to *m*-xylene without the formation of *p*-xylene. They also showed that *p*-xylene isomerizes five times as fast as *o*-xylene at 0°.[6] Brown and Jungk also studied the isomerization of xylenes.[7]

In the last two works above, molar quantities of catalyst were used to ensure having a homogeneous reaction and to prevent the decomposition of the *m*-xylene formed back to the starting materials. In the present work the relative rate constants for the decomposition of *m*-xylene were to be determined. Therefore it was desirable that the isomerizations proceed to the thermodynamic equilibrium of isomers rather than to pure *m*-xylene. This condition restricted us to the use of small quantities of catalyst and therefore to heterogeneous reaction conditions. For the sake of convenience we chose to use aluminum chloride as the catalyst.

Various xylene compositions were first isomerized without using a diluent. This had been done by McCaulay and Lien,[6] Baddeley[5] and Norris.[3] The trajectories of isomer compositions obtained could not be fitted by the equations described above. Since disproportionation was observed in

TABLE I

ISOMERIZATION DATA FOR XYLENE IN TOLUENE SOLUTION[a]

Rx. no.	Time, hr.	Isomer composition, mole % *o*-	*m*-	*p*-
1	0.0	99.9	0.0	0.1
	0.5	95.0	4.8	0.2
	1.0	84.6	14.8	0.6
	2.0	73.8	24.1	2.1
	3.0	63.2	32.8	4.0
	7.0	43.4	47.8	8.8
	20.0	19.0	63.2	17.8
	25.0	17.5	62.7	19.8
	44.0	18.7	60.2	21.1
2	0.0	0.5	98.6	0.9
	1.0	0.6	97.3	2.1
	2.0	2.6	93.3	4.1
	3.0	2.0	91.8	6.2
	5.0	4.6	86.0	9.4
	8.0	8.9	76.8	14.3
	12.0	11.4	70.9	17.7
	22.0	14.4	64.7	20.9
	46.0	17.4	60.9	21.7
3	0.0	0.1	0.5	99.3
	1.0	0.9	30.7	68.4
	1.5	2.7	38.9	58.4
	2.5	2.8	47.6	49.6
	4.0	3.8	55.8	40.4
	8.0	10.3	62.8	26.9
	20.0	15.1	62.8	22.1
	28.0	17.2	61.2	21.5
4	0.5	47.7	9.0	43.4
	1.0	44.1	15.6	40.2
	2.0	37.2	29.5	33.3
	3.0	33.1	40.1	28.8
	5.0	27.8	50.5	21.7
	7.0	25.0	54.7	20.3
	23.0	17.7	61.7	20.6

[a] The data from Table I are plotted on Fig. 1.

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[1] Presented in part in the Isomerization of Hydrocarbons Symposium, Division of Petroleum Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[2] R. H. Allen, T. Alfrey, Jr., and L. D. Yats, THIS JOURNAL, **81**, 42 (1959).

[3] J. F. Norris and D. Rubinstein, *ibid.*, **61**, 1163 (1939).

[4] K. J. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

[5] G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 101 (1952).

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

[7] H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

the above reactions, the isomerizations were then run in toluene solution in order to suppress disproportionation.

Xylene Isomerization in Toluene

The xylene isomer compositions were obtained by treating stirred 10 mole % solutions of xylenes in toluene at 50° with 5 mole % $AlCl_3$ in the presence of HCl. Infrared analysis of the xylenes in toluene solution proved impractical, due to the serious interference of the toluene absorption with the *o*-xylene absorption. Removal of the toluene by distillation proved impractical, since distillation invariably removed some of the xylene. The method of analysis finally used was a combination of vapor phase chromatography and infrared absorption. The toluene solutions were first analyzed for *o*-xylene using vapor phase chromatography and then analyzed for *m*- and *p*-xylenes by differential infrared analysis. The results obtained are given in Table I.

Calculation of the relative rate constant set from Fig. 1 was carried out in the following way. The most outstanding feature of Fig. 1 is the fact that the *p*-xylene trajectory starts asymptotically to the 0% *o*-xylene side, and the *o*-xylene trajectory starts asymptotically to the 0% *p*-xylene side. This feature shows that k_{po} and k_{op} are essentially equal to zero, as indicated by previous authors.[5-7] Of the six possible rate constants, two are equal to zero, and a third may be taken as equal to 1.0, since relative rate constants are being determined. Thus only three further parameters are needed to establish the complete set of relative rate constants. The equilibrium concentrations of the three isomers provide two parameters

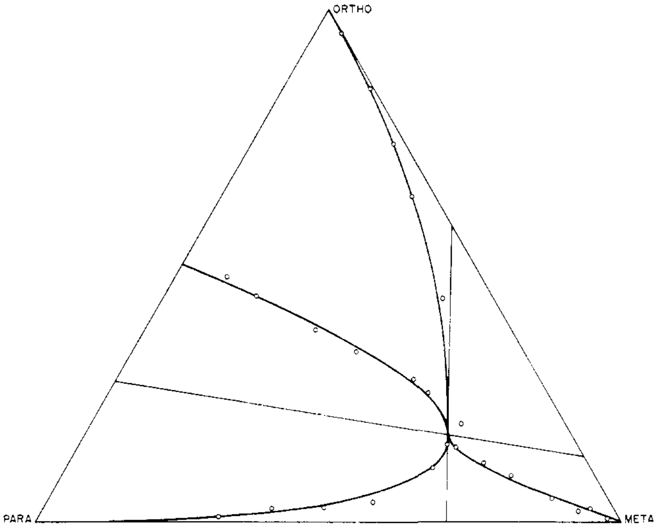

Fig. 1.—Xylene compositions obtained by $AlCl_3$ isomerization.

$$k_{om}O^* = k_{mo}M^*$$
$$k_{pm}P^* = k_{mp}M^*$$

and the shape of the isomerization trajectories provides the third parameter. The best set of relative rate constants and equilibrium mole percentages is

$$\begin{array}{lll} k_{po} = 0 & k_{om} = 3.6 & k_{mp} = 2.1 \\ k_{op} = 0 & k_{mo} = 1.0 & k_{pm} = 6.0 \\ O^* = 17 & M^* = 62 & P^* = 21 \end{array}$$

These rate constants generate the integrated rate expressions

For 100% *o*-xylene
$$O = 17 + 78.1e^{-4.12\tau} + 4.9e^{-8.58\tau}$$
$$P = 21 - 40.4e^{-4.12\tau} + 19.4e^{-8.58\tau}$$
For 100% *m*-xylene
$$O = 17 - 10.3e^{-4.12\tau} - 6.7e^{-8.58\tau}$$
$$P = 21 + 5.8e^{-4.12\tau} - 26.8e^{-8.58\tau}$$
For 100% *p*-xylene
$$O = 17 - 32.7e^{-4.12_\tau} + 15.7e^{-8.58\tau}$$
$$P = 21 + 17.6e^{-4.12} + 61.4e^{-8.58\tau}$$
For 50% *o*-xylene, 50% *p*-xylene
$$O = 17 + 22.7e^{-4.12\tau} + 10.3e^{-8.58\tau}$$
$$P = 21 - 11.5e^{-4.12\tau} + 40.5e^{-8.58\tau}$$

It was mentioned above that with $HF{\cdot}BF_3$, *p*-xylene isomerized five times as rapidly as *o*-xylene.[6] In that study, sufficient catalyst was used to complex all the xylene. In the present study the Al_2Cl_6 amounted to only 25 mole % of the xylenes, so the xylenes had to compete for the catalyst. Under these conditions, k_{pm}/k_{om} would be expected to be about one-third that found in the previous study, since *o*-xylene is three times as basic as *p*-xylene.[8] Thus k_{pm}/k_{om} would be expected to be equal to 5/3, which is fairly close to the value obtained in the present work. The accuracy of this calculation is questionable, especially since the basicity of the xylene toward $HF{\cdot}BF_3$ rather than $AlCl_3$ was used. But the calculation indicates that the results of the present kinetic study are consistent with the previous kinetic study.

Xylene Isomer Equilibrium.—In addition to permitting the estimation of the relative rate constants involved in the isomerization of xylenes, the present kinetic scheme offers a rather elegant technique for establishing the equilibrium concentration of xylene isomers with great accuracy. On Fig. 1 are shown two straight lines intersecting at the equilibrium point determined in this work. The integrated kinetic expressions derived predict that any composition lying on these lines will isomerize in a straight line trajectory of compositions to the equilibrium point. Experimentally these should sufficiently approximate straight lines so that the isomerization of four xylene isomer distributions would permit a measure of the equilibrium distribution that is limited only by the accuracy of the analyses and not by the necessity of obtaining complete equilibrium. Essentially this was done with cymenes[2] and should be possible to do with any three-compound equilibration that involves rate steps that are first order, pseudo-first order or of the type described in the previous paper of this series.[2]

We had expected that the xylene isomer equilibrium we obtained would be higher in *m*-xylene than the thermodynamic equilibrium, due to selective complexing of the *m*-xylene by the

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[8] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

TABLE II

Temp., °C.	Catalyst	*m* Catalyst/ *m* xylene	Mole % xylene *o*	*m*	*p*	Ref.
50	$Al_2Cl_6 \cdot HCl$	0.50	15	68	17	3
50	$Al_2Br_6 \cdot HBr$	.05	13	71	16	4
82	$HF \cdot BF_3$	.09	15	64	22	6
100	$HF \cdot BF_3$	.08	19	61	20	6
121	$HF \cdot BF_3$	.13	18	60	21	6
27			16	60	24	9
50	Al_2Cl_6HCl	.25	17	62	21	*loc. cit.*

$AlCl_3$ used. In Table II, comparison of our equilibrium to those previously reported provides no evidence for selective complexing. Thus, although the selectivity of $AlCl_3$ for *m*-xylene at 0° has been reported,[10] no such selectivity is evident at 50°.

Mechanism of Xylene Isomerization.—The fact that $k_{po} = k_{op} = 0$ for the isomerization in toluene solution confirms the postulated intramolecular 1,2-shift mechanism for the isomerization of xylenes.

Most carbonium ion type rearrangements are believed to involve the shift of an alkyl group with its pair of electrons. The Friedel–Crafts isomerization of alkylbenzenes, on the other hand, is pictured to involve an alkyl group shifting without its pair of electrons, *i.e.*, a carbonium ion shifting. The carbonium ion shift is postulated for two reasons. First, the alkyl group mobility in the Friedel–Crafts reaction parallels the carbonium ion stability. Second, the mechanism for the disproportionation of alkyl benzenes most likely involves a nucleophilic attack by an aromatic ring on an electron deficient alkyl group.

The carbonium ion shift mechanism recently has received support in a cymene isomerization study.[2] Since it was shown that $k_{po} \neq 0$ and $k_{op} \neq 0$ in the isomerization of cymenes, the isopropyl group must dissociate appreciably from the aromatic ring during the isomerization. Dissociation of the isopropyl group as a carbonium ion appears the most plausible.

The kinetics of xylene isomerization, on the other hand, indicate that the methyl group never dissociates appreciably from the aromatic ring during the isomerization. This fact and the fact that the isomerization of xylenes proceeds much more readily than the disproportionation of xylenes[5,6,11] suggests that the activated complex for isomerization differs significantly from that for disproportionation. These considerations suggest that the isomerization of xylenes may well proceed by the more common mechanism for a carbonium ion type rearrangement, the shift of the methyl group *with* its pair of electrons.

Xylene Isomerization Absolute Rates.—It has been shown that when a dilute solution of cymenes is isomerized with $AlCl_3$, neither first-order nor pseudo-first-order kinetics is followed.[2] Indeed, since the interaction of $AlCl_3 \cdot HCl$ with alkylaromatics generally forms an insoluble oily phase of a complicated nature, and sampling the reaction mixture would be expected to change the catalyst–hydrocarbon ratio, clean cut absolute rates are not expected. Therefore it is rather surprising that the xylene isomerizations reported above are pseudo-first order. The significance of this result is being studied and will be reported on in a future paper.

Xylene Isomerization without Solvent

The xylene isomer compositions were obtained by treating stirred xylenes at 50° with 25 mole % $AlCl_3$ in the presence of HCl. The infrared analyses for these compositions are plotted as the open circles on Fig. 2. The combination vapor phase chromatography:infrared absorption analyses are plotted as the closed circles. The lines are reproductions of the theoretical curves obtained from the xylene isomerizations in toluene solution. The fact that three out of four trajectories fit the theoretical curves for at least the first half of the reactions is further evidence that toluene did not appreciably affect the previous isomerizations.

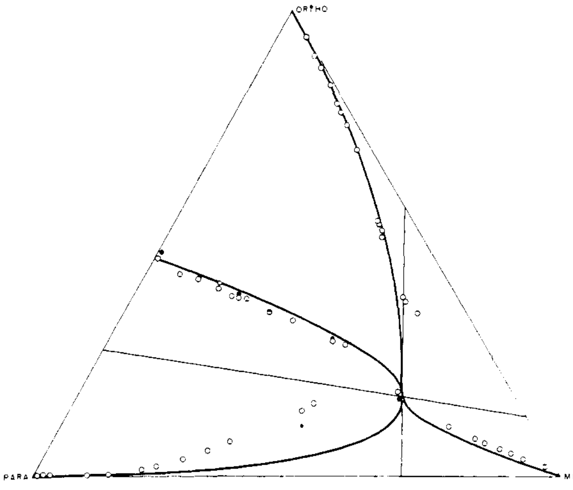

Fig. 2.—Xylene compositions obtained by $AlCl_3$ isomerization.

The reason that the *p*-xylene isomerization compositions deviate seriously from the theoretical curve is evident from consideration of Fig. 3,[12]

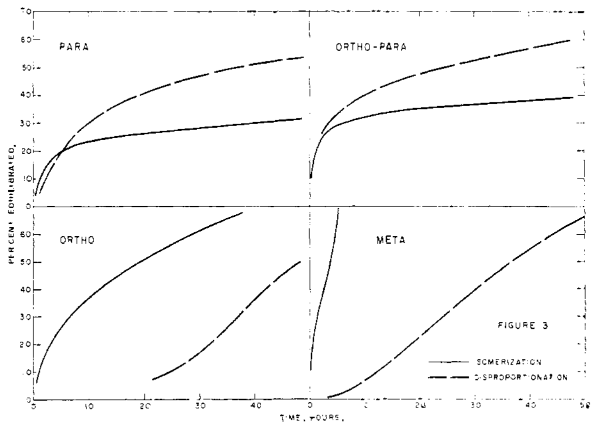

Fig. 3.

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[9] W. J. Taylor, *et al.*, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

[10] J. H. Waals, *et al.*, U. S. Patent 2,842,604 (1958).

[11] A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953).

[12] The per cent. equilibrated for disproportionation was taken as the mole % toluene divided by 0.25; K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

p-xylene disproportionates far more readily than either *o*- or *m*-xylene. The three-compound kinetic equations presented earlier are not valid when disproportionation occurs.

Although the *p*-xylene trajectory deviates seriously when no diluent is used, the fact that $k_{po} = 0$ in toluene solution indicates that the isomerization of *p*-xylene in toluene solution is intramolecular. If *p*-xylene alkylated toluene, it is doubtful that k_{po} would equal zero. The postulate that *p*-xylene will readily alkylate itself, but not toluene, is consistent with the fact that toluene is less susceptible to electrophilic substitution than *p*-xylene.[13]

The agreement of the *o*-xylene–*p*-xylene isomerization compositions with the theoretical trajectory in spite of extensive disproportionation suggests that the disproportionation reaction is largely the alkylation of the *o*-xylene by the *p*-xylene.

The dramatically higher ratio of disproportion rate to isomerization rate for *p*-xylene as compared to *o*-xylene or *m*-xylene is quite surprising since *p*-xylene is the least readily substituted isomer. Thus, *p*-xylene appears to have a great tendency to act as an alkylating agent.

Experimental

To a solution of 663 g. (7.2 moles) of toluene and 85 g. (0.8 mole) of xylene maintained at 50° in 2-l. 3-necked creased flask, equipped with a gas inlet tube, a thermometer, a stirrer and a $CaCl_2$ drying tube, was added 53 g. (0.4 mole) of Baker and Adams resublimed anhydrous $AlCl_3$. Hydrogen chloride was passed through the stirred reaction mixture for 10 minutes. At specific times 50-ml. samples were withdrawn from the reaction mixture, washed with water and dried over $CaSO_4$. The samples were then analyzed by vapor phase chromatography[14] using a 10 ft. column at 90° packed with 30% di-(2-ethylhexyl) sebacate and 70% 30-60 mesh Celite. The V.P.C. unit was connected through a Brown Recorder to an Instron two counter automatic integrator. One area for *m*- and *p*-xylenes and one area for *o*-xylene were obtained. The analyses were repeated until analyses differing no greater than 1% were obtained. Since an equivalent amount of *p*-xylene produced an area 1.053 times that for *o*-xylene and an equivalent amount of *m*-xylene produced an area 1.022 times that for *o*-xylene, it was necessary to use the differential infrared analyses for *m*- and *p*-xylene to adjust the *m*-, *p*-xylene areas so that the *o*-xylene analyses could be calculated.

The isomerizations of xylene without toluene were carried out as above, except that 424 g. (4.0 moles) of xylene and 133 g. (1.0 moles) of $AlCl_3$ were added to a one-l. flask, and only 10-ml. samples were taken. The samples were analyzed by infrared analysis.

Acknowledgment.—The authors are indebted to D. S. Erley of the Dow Spectroscopy Department for the infrared data.

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[13] F. E. Condon, THIS JOURNAL, **74**, 2528 (1952); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

[14] R. S. Gohlke, *Anal. Chem.*, **29**, 1723 (1957).

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Counterion Binding by Polyelectrolytes. II. The Determination of the Binding of Univalent Cations by Long-chain Polyphosphates from Conductivity and Electrophoresis Data[1]

BY ULRICH P. STRAUSS AND SYDNEY BLUESTONE

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The conductivities of long-chain lithium, sodium, potassium and tetramethylammonium polyphosphate samples were measured in 0.2 *M* solutions of the bromides of the corresponding cations at 0°. The equivalent conductance of each polyphosphate was independent of the polyphosphate concentration. By combining the equivalent conductance data with the corresponding electrophoretic mobilities, the degree of ionization, *i*, of each of the polyphosphates was calculated by means of the Kohlrausch equation. The resulting values of *i* were proportional to the values of the electrophoretic mobility. These experimental results are consistent with the interpretation that the polyphosphate chains are free draining, that relaxation effects are negligible and that the friction coefficient of the polymer is not affected by the nature of the bound counterion within the range of counterion sizes employed in this investigation.

In several recent papers, theories concerning the electrophoretic mobility[2,3] and the electrical conductivity[4] of polyelectrolytes in solutions containing a simple electrolyte have been developed. Experimental results conforming qualitatively to the electrophoresis theory have also been reported.[5] If the polyelectrolyte chains are free-draining, u, the electrophoretic mobility, is given by the expression

$$u = e/f \qquad (1)$$

where e and f are the effective charge and friction constant, respectively, of a monomer unit.[2,3] This result has been used in the first paper of this series to estimate the degree of ionization of polyphosphates in solutions of tetramethylammonium (TMA$^+$) and alkali metal bromides.[6] The validity of eq. 1 depends on the absence of relaxation effects. Such relaxation effects have been considered insignificant both on theoretical[2] and experimental[5] grounds. On the other hand, Longworth and Hermans[7] have theorized relaxation effects to explain qualitatively observed deviations of their experimental conductivity results from the

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[1] This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018. The results presented in this paper will be contained in a thesis to be presented by S. Bluestone to Rutgers, The State University, in partial fulfillment of the requirements for the Ph.D. degree.

[2] J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.*, **75**, 543 (1956).

[3] J. J. Hermans and H. Fujita, *Koninkl. Ned. Akad. Wetenshap, Proc.*, *B***58**, 182 (1955).

[4] H. Fujita and J. J. Hermans, *ibid.*, *B***58**, 188 (1955).

[5] N. Nagasawa, A. Soda and I. Kagawa, *J. Polymer Sci.*, **31**, 439 (1958).

[6] U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

[7] R. Longworth and J. J. Hermans, *J. Polymer Sci.*, **26**, 47 (1957).