# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, MIDLAND DIVISION, THE DOW CHEMICAL CO., MIDLAND, MICH.]

## Kinetics of Three-compound Equilibrations. III. The Isomerization of Ethyltoluene

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RECEIVED DECEMBER 2, 1959

The isomerization of ethyltoluene was studied as a three-compound equilibration involving six rate constants. Dilute solutions of five ethyltoluene isomer distributions in toluene were isomerized at room temperature with aluminum chloride. In each case samples were taken periodically and analyzed by differential infrared spectroscopy and vapor phase chromatography. The isomer distributions obtained are consistent with the following relative rate constants and equilibrium percentages: $k_{po} = 1.0$, $k_{op} = 2.9$, $k_{mo} = 5.3$, $k_{om} = 38.2$, $k_{pm} = 60.8$, $k_{mp} = 24.6$, $O^* = 9.0$, $M^* = 64.8$, $P^* = 26.2$. This work shows that the mechanism of isomerization of ethyltoluenes under these conditions is not exclusively an intramolecular 1,2-shift, as was the case with xylenes. From the magnitude of $k_{pa}$ and $k_{op}$ it appears likely that most of the isomerization proceeds by an intramolecular 1,2-shift.

### Introduction

It has been shown[1] that for certain three-compound equilibrations involving six rate constants, as

$$\begin{tikzcd}
 & \textit{ortho} \arrow[dl, shift right, "k_{op}"'] \arrow[dr, shift left, "k_{om}"] & \\
\textit{para} \arrow[ur, shift right, "k_{po}"'] \arrow[rr, shift left, "k_{pm}"] & & \textit{meta} \arrow[ul, shift left, "k_{mo}"] \arrow[ll, shift left, "k_{mp}"]
\end{tikzcd}$$

the integrated rate expressions are

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

where $O(t)$ is the concentration of the *ortho* isomer at time $t$, $O^*$ is the equilibrium concentration of the *ortho* isomer, $A$ and $B$ are determined from the starting concentrations, $\alpha$ and $\beta$ from the rate constant set, and $\tau$ is some function of time. The use of this scheme for the study of isomerization of cymenes[1] and xylenes[2] has been reported. The use of this scheme for the study of the isomerization of ethyltoluenes is now being reported.

Much literature has appeared on the ethylation of aromatics[3] and the disproportionation of ethylaromatics,[4] but very little has been reported on the isomerization of ethylaromatics. The fact that *o*-ethyltoluene isomerizes is an important feature of the Dow vinyltoluene process.[5] The thermodynamic equilibrium of ethyltoluene isomers in the vapor phase has been calculated to contain 8% *o*-, 48% *m*- and 44% *p*-ethyltoluene.[6] The isomer distributions obtained by the continuous ethylation of toluene with various catalyst have been reported.[7] These distributions probably differ only in the extent of isomerization that accompanies the alkylation, since the distributions appear to be consistent with the results of the present work. One of the distributions, 11% *o*-, 64% *m*- and 25% *p*-, is quite close to the distribution taken to be the equilibrium distribution in the present work. One experiment has been reported on the isomerization of ethyltoluene *per se*. Brown has shown that the relative rates of Friedel–Crafts isomerization of alkyltoluenes decrease in the order isopropyltoluene > ethyltoluene > xylene.[8]

### Experimental

**Materials.**—Redistilled commercial grade toluene was used.

The *o*-ethyltoluene was obtained from the Dow vinyltoluene plant. Comparison with an A.P.I. sample by infrared analysis showed no significant difference.

Clemmensen reduction of recrystallized[9] Eastman Kodak Co. *p*-methylacetophenone produced *p*-ethyltoluene, which when treated with concentrated sulfuric acid, washed and distilled showed no significant impurities.

The preparation of *m*-ethyltoluene was patterned after the process of Schlatter for separation of *m*- and *p*-xylenes.[10] A mixture of *m*- and *p*-ethyltoluenes obtained from the Dow vinyltoluene plant was exhaustively *t*-butylated at 35° with isobutylene using $BF_3{\cdot}H_2O$ as the catalyst. The 3-ethyl-5-*t*-butyltoluene obtained by distillation of the alkylate was then cracked at 300° over a Houdry S-65 silica–alumina catalyst. Distillation of this product yielded *m*-ethyltoluene that was analyzed by infrared to contain 1% *o*- and 1% *p*-ethyltoluenes.

Baker and Adams reagent anhydrous aluminum chloride was used with Matheson anhydrous hydrogen chloride.

**Isomerization Procedure.**—To a one-liter 3-necked creased flask, equipped with a gas inlet tube, thermometer, stirrer and a water trap connected to the flask through a calcium chloride drying tube, was added 450 g. (4.9 moles) of toluene and 5.4 g. (0.041 mole) of aluminum chloride. Through the stirred reactants at room temperature was passed anhydrous hydrogen chloride for 5 minutes. To this solution at room temperature was added 50.0 g. (0.41 mole) of ethyltoluene. At specific times, 25-ml. portions of the reaction mixture were withdrawn, quenched, washed and dried. The *p*-ethyltoluene isomerization was run on a $^3/_4$ scale in a one-liter flask. The 85% *p*-, 15% *o*-ethyltoluene isomerization was run on a $^3/_{10}$ scale in a 500-ml. flask.

**Analytical Procedure.**—The samples, untreated and undiluted, were scanned on a double beam infrared spectrom-

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

[2] R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).

[3] E. M. Hodnett and C. F. Feldman, *ibid.*, **81**, 1638 (1959); C. C. Lee, M. C. Hamblin and N. James, *Can. J. Chem.*, **36**, 1597 (1958); C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245, 6249 (1956).

[4] R. M. Roberts, G. A. Ropp and O. K. Neville, *ibid.*, **77**, 1764 (1955); M. C. Hoff, *ibid.*, **80**, 6046 (1958); D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956); W. J. Roberts and M. B. Price, First Regional Meeting, Delaware Valley Section, A.C.S., Feb., 1956.

[5] R. H. Boundy and R. F. Boyer, "Styrene," A.C.S. Monograph No. 115, Reinhold Publishing Corp., New York, N. Y., 1952, p. 1232; J. L. Amos and K. E. Coulter, U. S. Patent 2,763,702 (Sept. 18, 1956).

[6] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **37**, 95 (1946).

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[8] H. C. Brown and H. Jungk, THIS JOURNAL, **77**, 5579 (1955).

[9] W. M. Schubert, J. Robins and J. L. Haun, *ibid.*, **79**, 910 (1957).

[10] M. J. Schlatter, U. S. Patent 2,734,930 (Feb. 14, 1956).

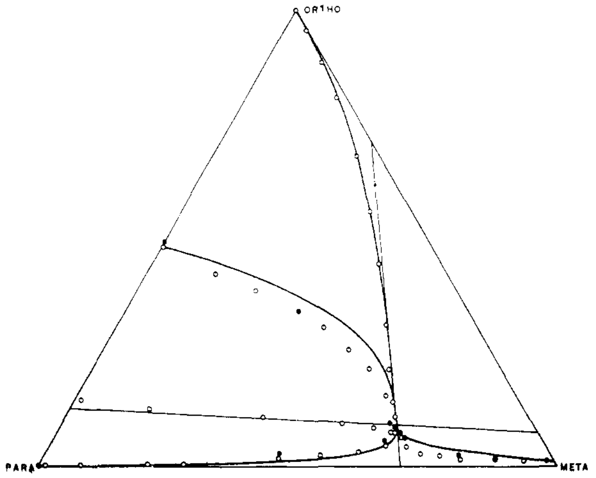

Fig. 1.—Ethyltoluene isomer distributions obtained by $AlCl_3$ isomerization: O, infrared data; ●, v.p.c. data.

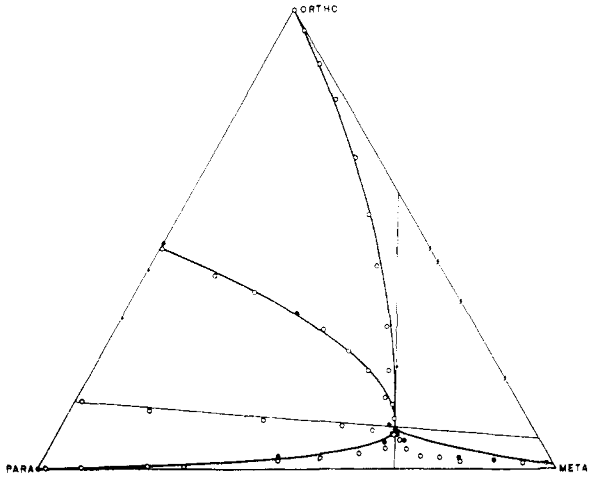

Fig. 2.—Ethyltoluene isomer distributions obtained by $AlCl_3$ isomerization: O, infrared data; ●, v.p.c. data.

eter[11] with the toluene absorptions of the sample matched out. The instrument automatic gain feature[11] was used to compensate for the low optical energy in regions of high toluene absorption. Standard absorbances for each isomer at 12.24, 12.78 and 13.25 $\mu$ were determined using a straight line between the absorption minima at 11.8 and 14.1 $\mu$ for the base line. Three absorbances at the analytical wave lengths were determined for each sample and introduced into a set of three simultaneous linear equations involving the nine standard absorbances. The equations were then solved for concentrations using a Royal McBee LGP-30 computer. This calculation assumes a straight line relation between absorbance and concentration.

To check the accuracy of the method a synthetic mixture was analyzed with the result

| Toluene, % | Known | Found |
|---|---|---|
| *o*-Ethyl- | 10.0 | 9.3 |
| *m*-Ethyl- | 59.0 | 59.0 |
| *p*-Ethyl- | 31.0 | 31.7 |

The *m*- and *p*-ethyltoluene determinations are within the estimated error of ±3% of the amount present. Since the broad *m*-ethyltoluene absorbtion overlaps the *o*-ethyltoluene absorbtion, several samples low in *o*-isomer were also analyzed by vapor phase chromatography.

The v.p.c. analyses were carried out at 115° using a 10-ft. column packed with Craig polyester adipate on Chromosorb W. The instrument[12] was connected through a Brown Recorder to an Instron two counter automatic integrator. One peak for *m*- and *p*-ethyltoluenes and one peak for *o*-ethyltoluene was obtained. The infrared analyses indicate an equilibrium value of 7.5% *o*-, while the vapor phase chromatography analyses indicate an equilibrium value of 9.0% *o*-ethyltoluene.

Selective complexing of ethyltoluene by the catalyst evidentally did not significantly alter the equilibrium composition of isomers, since the analysis for the last sample was identical to the analysis for the residue in each isomerization.

## Results and Discussion

The experimental isomer compositions are presented in Table I and plotted as the points on Figs. 1 and 2.

The determination of a relative rate constant set for a three-compound equilibration must provide five rate constants, since one will be set equal to 1.0. The three equilibrium constants involved provide three parameters, so that only two further parameters are required. In the cymene case,[1] the fact that the *ortho* trajectory was a straight line indicated that $k_{po} = k_{mo}$, so that only one parameter was varied in order to fit the data to the theoretical equations. In the xylene case,[2] it was evident that $k_{po} = k_{op} = 0$, so that only one parameter was varied. In the ethyltoluene case presented here, unfortunately, it was necessary to vary two parameters, so that the rate constants are more arbitrary than those for the previous two cases.

Haag and Pines have pointed out that for an appropriate three-compound equilibration, tangents at the 100% point for each of the three isomerization composition trajectories must intersect at a common point.[13] Although this observation is helpful in obtaining a rough approximation of the rate constants, it didn't provide a sufficiently accurate additional parameter.

The best relative rate constant set found based on the assumption that $k_{po} = k_{op} = 0$ is

$k_{pm} = 17.3$ $k_{om} = 7.2$ $\alpha = 1.0$
$k_{mp} = 7.0$ $k_{mo} = 1.0$ $\beta = 3.19$
$O^* = 9.0$ $M^* = 64.8$ $P^* = 26.2$

This set generated the curved lines on Fig. 1.

The correlation with the experimental isomer distributions is rather poor, which suggests that the isomerization of ethyltoluenes under the conditions used here does not proceed exclusively by an intramolecular 1,2-shift.

By varying both parameters the best relative rate constant set found is

$k_{po} = 1.0$ $k_{mo} = 5.3$ $k_{pm} = 60.8$
$k_{op} = 2.9$ $k_{om} = 38.2$ $k_{mp} = 24.6$
$O^* = 9.0$ $P^* = 26.2$ $M^* = 64.8$

This set produces the following integrated equations for the percentage of *ortho* and *para* isomers in terms of the parameter $\tau$, where

$$\tau = \int_0^t f(t)dt$$

some unknown function of time.

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[11] L. W. Herscher, H. D. Ruhl and N. Wright, *J. Opt. Soc. Am.*, **48**, 36 (1958).

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

[13] W. O. Haag and H. Pines, Isomerization and Related Processes Symposium, Division of Petroleum Chemistry Preprints, 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

TABLE I

ISOMERIZATION DATA FOR ETHYLTOLUENE IN TOLUENE

| Rx. no. | Time, min. | Isomer composition, mole % *p*- | *m*- | *o*-[a] | *o*-[b] |
|---|---|---|---|---|---|
| 1 | 0 | 98.6 | 1.2 | 0.2 | 0.0 |
| | 1 | 91.5 | 8.3 | .2 | |
| | 5 | 78.7 | 20.9 | .4 | |
| | 15 | 71.6 | 27.8 | .6 | |
| | 45 | 52.8 | 45.4 | 1.9 | 2.9 |
| | 90 | 44.2 | 53.5 | 2.3 | |
| | 180 | 36.3 | 60.5 | 3.2 | |
| | 360 | 30.7 | 64.8 | 4.5 | 5.8 |
| | 1440 | 26.8 | 67.1 | 6.1 | 7.6 |
| | Res. | 26.8 | 66.9 | 6.3 | |
| 2 | 0 | 83.9 | 1.4 | 14.8 | |
| | 5 | 71.9 | 15.5 | 12.5 | |
| | 45 | 51.2 | 38.2 | 10.7 | |
| | 180 | 36.5 | 54.1 | 9.4 | |
| | 360 | 31.1 | 60.3 | 8.5 | |
| | 720 | 27.6 | 64.7 | 7.7 | 9.5 |
| | 1440 | 27.2 | 65.8 | 7.0 | 8.7 |
| | Res. | 27.3 | 65.9 | 6.8 | |
| 3 | 0 | 51.7 | 0.3 | 48.0 | 49.1 |
| | 5 | 44.2 | 13.6 | 42.1 | |
| | 15 | 38.5 | 22.9 | 38.5 | |
| | 45 | 32.7 | 33.2 | 34.0 | 33.9 |
| | 90 | 29.6 | 40.1 | 30.3 | |
| | 180 | 27.2 | 47.2 | 25.6 | |
| | 360 | 25.6 | 53.1 | 21.3 | |
| | 720 | 25.0 | 59.6 | 15.4 | |
| | 1440 | 25.5 | 63.6 | 10.9 | |
| | 2880 | 26.4 | 65.8 | 7.8 | |
| | Res. | 27.0 | 65.2 | 7.7 | |
| 4 | 0 | 0.0 | 0.0 | 100.0 | |
| | 1 | .2 | 4.1 | 95.7 | |
| | 5 | .9 | 10.9 | 88.2 | |
| | 15 | 1.9 | 17.4 | 80.7 | |
| | 45 | 4.5 | 27.6 | 67.9 | |
| | 90 | 8.0 | 36.4 | 55.6 | |
| | 180 | 12.0 | 43.8 | 44.2 | |
| | 360 | 17.1 | 51.8 | 31.1 | |
| | 720 | 21.5 | 57.2 | 21.3 | |
| | 1440 | 24.4 | 61.5 | 14.1 | |
| | 6900 | 27.6 | 65.1 | 7.3 | |
| | Res. | 26.7 | 66.3 | 7.0 | |
| 5 | 0 | 1.1 | 97.8 | 1.2 | 1.2 |
| | 1 | 1.5 | 97.2 | 1.3 | |
| | 5 | 5.7 | 93.1 | 1.2 | |
| | 15 | 11.1 | 87.5 | 1.4 | 1.7 |
| | 45 | 17.6 | 80.8 | 1.6 | 2.6 |
| | 90 | 21.3 | 76.2 | 2.5 | |
| | 180 | 24.6 | 72.5 | 2.8 | |
| | 360 | 26.7 | 69.0 | 4.2 | 6.2 |
| | 1440 | 26.7 | 66.7 | 6.6 | |
| | Res. | 26.4 | 66.9 | 6.7 | |

[a] Differential infrared analyses. [b] Normalized vapor phase chromatography analyses.

Starting with 100% para

$$\%\ \textit{ortho} = 9.0 - 15.7e^{-\tau} + 6.7e^{-2.0\tau}$$
$$\%\ \textit{para} = 26.2 + 8.1e^{-\tau} + 65.7e^{-2.0\tau}$$

Starting with 85% *para*, 15% *ortho*

$$\%\ \textit{ortho} = 9.0 + 6.0e^{-2.0\tau}$$
$$\%\ \textit{para} = 26.2 + 58.8e^{-2.0\tau}$$

Starting with 52% *para*, 48% *ortho*

$$\%\ \textit{ortho} = 9.0 + 34.6e^{-\tau} + 4.4e^{-2.0\tau}$$
$$\%\ \textit{para} = 26.2 - 18.0e^{-\tau} + 43.8e^{-2.0\tau}$$

Starting with 100% *ortho*

$$\%\ \textit{ortho} = 9.0 + 89.0e^{-\tau} + 2.0e^{-2.0\tau}$$
$$\%\ \textit{para} = 26.2 - 45.7e^{-\tau} + 19.5e^{-2.0\tau}$$

Starting with 1% *ortho*, 99% *meta*

$$\%\ \textit{ortho} = 9.0 - 5.0e^{-\tau} - 2.9e^{-2.0\tau}$$
$$\%\ \textit{para} = 26.2 + 2.6e^{-\tau} - 28.8e^{-2.0\tau}$$

The lines shown on Fig. 2 were obtained from these equations.

The fit is reasonable with all but the 99% *meta* trajectory. We have no reasonable explanation for this incongruity.

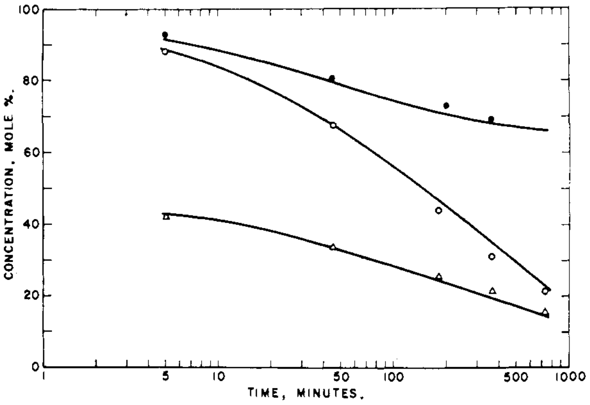

Fig. 3.—●, % *m*-ethyltoluene in Rx. 5; ○, % *o*-ethyltoluene in Rx. 4; △, % *o*-ethyltoluene in Rx. 3.

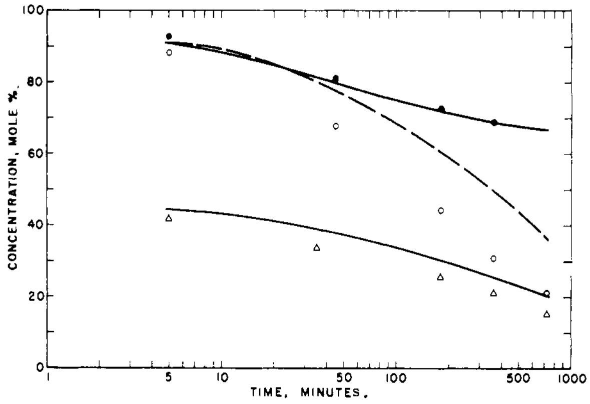

Fig. 4.—●, % *m*-ethyltoluene in Rx. 5; ○, % *o*-ethyltoluene in Rx. 4; △, % *o*-ethyltoluene in Rx. 3.

**Absolute Rates.**—If the rate steps involved in the isomerization were first order or pseudo first *order*, $\tau$ would be a linear function of time. By solving for $\tau$ in the above theoretical equation for each experimental mole % of *p*-ethyltoluene obtained in the 85% *p*-, 15% *o*-trajectory, the following values for $\tau$ and the times to which they correspond are obtained. The isomerization rate steps are evidentally not first order or pseudo first order, since $\tau$ does not appear to be a linear function of time.

| Time, min. | 5 | 45 | 180 | 360 | 720 | 1440 |
|---|---|---|---|---|---|---|
| $\tau$ | 0.13 | 0.43 | 0.87 | 1.24 | 1.86 | 2.54 |

The deviation in rate, as in the cymene case,[1] is probably due to the formation of some highly basic material. A similar explanation has been offered for the deactivation of catalyst in the methylation of methyl aromatics.[14] Although the degree of deviation from first-order kinetics, *i*-propyl > ethyl > methyl, correlates inversely with basicity, the basicity differences alone are probably not large enough to account for the rate deviations. It seems more likely that the rate deviations are due to alkyl hydrogen transfer and cracking reactions.[15]

If the above values for $\tau$ are introduced into the equations for three of the four remaining trajectories, the curved lines shown on Fig. 3 are obtained. The points represent the experimental data. The agreement indicates that the relation of $\tau$ to time is fairly consistent from one reaction mixture to another. That is, although the reactions are not pseudo first order, their deviation from a pseudo-first-order rate are somewhat reproducible.

If the above treatment is applied to the equations from the rate constant set in which $k_{po} = k_{op} = 0$, Fig. 4 is obtained. The 100% *p*-trajectory was not included in either figure because its deviation from the experimental data obscured the figures without adding any useful information. If any conclusion may be drawn from the deviation of the 100% *o*-trajectory in Fig. 4, the most reasonable conclusion would be that the ratio of $\beta$ to $\alpha$ is more accurate from the rate constants set for Fig. 3 than the rate constant set for Fig. 4. Thus, the absolute rate data tends to support the thesis that the isomerization of ethyltoluenes is not exclusively an intramolecular 1,2-shift.

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[14] W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

[15] We wish to thank Dr. D. A. McCaulay for this explanation.

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# Kinetics of Three-compound Equilibrations. IV. The Isomerization of Alkylaromatics

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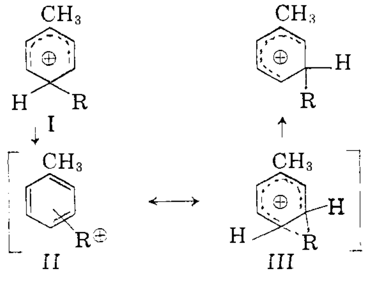
RECEIVED DECEMBER 2, 1959

The isomerization of xylene in toluene solution by the action of $AlCl_3 \cdot HCl$ has been shown to proceed by an intramolecular 1,2-shift. The present work provides evidence that under the above conditions, the isomerization of *t*-butyltoluenes proceeds by alkylation of the toluene, and the isomerization of ethyltoluenes and isopropyltoluenes proceed by both mechanisms.

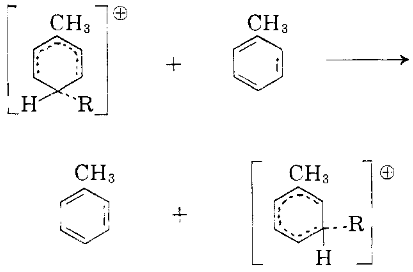
## Introduction

Data presented in this paper indicate that the Friedel–Crafts positional isomerization of alkyltoluenes in toluene proceeds by either an intramolecular 1,2-shift mechanism, an alkylation–dealkylation mechanism, or both. The alkyl shift mechanism has been offered for the isomerization of xylenes.[1] The alkyl transfer mechanism is here offered for the isomerization of *t*-butyltoluenes, and a combination of both mechanisms for ethyltoluenes ane isopropyltoluenes.

The intramolecular 1,2-shift mechanism may be pictured as



The alkyl group of the aromatic $\sigma$-complex bridges two adjacent aromatic carbons and then swings over to its final position. Loss of proton yields the product. The intermolecular mechanism may be pictured as is shown in the next diagram. Nucleophilic attack by a second aromatic on the electronically deficient alkyl group of the $\sigma$-complex displaces the first aromatic ring. Loss of proton from the second aromatic ring yields the product. This mechanism is quite similar to that proposed for the disproportionation of alkylaromatics.[2]



**Isomerization of *t*-Butyltoluene.**—The postulate that *t*-butylaromatics isomerize by alkylation-dealkylation is supported by the ease with which *t*-butyl groups split off of molecules under acidic conditions; for example, from *t*-butylbenzene[2c] and methyl pentamethylethyl ketone.[3] More direct evidence for the present argument has been reported by Schlatter.[4] The hydrogen fluoride-catalyzed reaction of 3,5-di-*t*-butylethylbenzene with toluene produced *m*-*t*-butylethylbenzene that was better than 90% pure. Thus *t*-butyl groups

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[1] (a) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952); (b) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952); (c) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

[2] (a) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955, p. 528; (b) A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953); (c) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953); (d) R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

[3] H. D. Zook, W. E. Smith and J. L. Greene, *ibid.*, **79**, 4436 (1957).

[4] M. J. Schlatter, U. S. Patent 2,768,985 (Oct. 30, 1956).