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ISOMERIZATION OF BROMOTOLUENES UNDER THE INFLUENCE OF $Al_2Br_6.HBr$

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Abstract—The isomerization of the bromotoluenes in radioactive toluene with $Al_2Br_6.HBr$ as a catalyst was investigated. The isomerizations *ortho–para* and *para–ortho* are completely *inter*molecular, and are in agreement with the catalytic bromination mechanism given by Olah. The isomerization and formation of the *meta*-bromotoluene involve an *intra*molecular 1,2-shift.

INTRODUCTION

THE study on the mechanism of the Friedel–Crafts reaction made under the guidance of the late F. L. J. Sixma[1–4] has been extended and this work deals with the isomerization of the bromotoluenes under the influence of $Al_2Br_6.HBr$.

Olah and Meyer[5] studied the isomerization of the bromotoluenes with water-promoted Al_2Cl_6 in the absence of solvent. They found an *inter*molecular isomerization of *ortho* and *para*-bromotoluene, but in the isomerization of *meta*-bromotoluene they could not decide between an *intra*molecular 1,2-shift or an *inter*molecular mechanism.

Crump and Gornowicz[6] investigated the isomerization of the bromotoluenes with anhydrous aluminium bromide in the presence and absence of solvents (especially toluene). According to these authors there is some indication that even in the presence of a large excess of toluene *meta*-bromotoluene formation and isomerization occurs predominantly via an *intra*molecular 1,2-shift. In the absence of solvent Crump and Gornowicz propose a complete *intra*molecular mechanism.

Kooyman and Louw[7] state that the transbromination experiments with bromobenzene and toluene initially produce *ortho* and *para*-bromotoluene in comparable amounts, but no mention is made of the formation of the *meta*-isomer. In order to distinguish between the *intra*- or *inter*molecular isomerization of the bromotoluenes, the reaction was carried out in labelled toluene. *Inter*molecular isomerization results in radioactive bromotoluene, *intra*molecular isomerization gives no increase in activity.

METHOD AND RESULTS

The *inter*- and *intra*molecular isomerization reactions were carried out in toluene-1-^{14}C at 0°. The catalyst, Al_2Br_6 was saturated with hydrogen bromide. Since heterogeneous reactions are irreproducible, the catalyst concentration was kept low enough to ensure a homogeneous reaction medium. In all experiments the ratio catalyst: bromotoluene:toluene-1-^{14}C was 1:100:200. Moisture was carefully excluded. Samples were taken periodically and quenched in a 5% NaOH solution. With preparative GLC the crude samples were separated into toluene and the bromotoluenes. The bromotoluenes were analysed by GLC but could not be separated on a preparative scale. For radioactive assay the bromotoluenes were therefore converted into the xylenes which can be separated by preparative GLC (see Experimental). The results of typical experiments are given in Tables 1, 2 and 3.

Table 1. Isomerization of *ortho*-bromotoluene in radioactive toluene with $Al_2Br_6.HBr$ as a catalyst, at 0°

Sample	Reaction time in min	% *ortho*	% *meta*	% *para*	Total activity ($o + m + p$) in cts/mmol.s.
1.	10	86·6%	5·1%	8·3%	80·1
2.	20	80·1%	7·2%	12·7%	126·0
3.	30	73·5%	11·1%	15·4%	154·2
4.	40	70·7%	11·8%	17·4%	168·0
5.	50	68·2%	12·8%	19·0%	180·0

Table 2. Isomerization of *para*-bromotoluene in radioactive toluene with $Al_2Br_6.HBr$ as a catalyst, at 0°

Sample	Reaction time in min	% *ortho*	% *meta*	% *para*	Total activity ($o + m + p$) in cts/mmol.s.
1.	5	8·5%	4·9%	86·6%	64·9
2.	10	16·5%	6·8%	76·7%	124·2
3.	15	23·9%	10·1%	66·0%	174·6
4.	25	28·2%	14·2%	57·6%	197·1
5.	30	33·5%	18·0%	48·5%	231·6

Table 3. Isomerization of *meta*-bromotoluene in radioactive toluene with $Al_2Br_6.HBr$ as a catalyst, at 0°

Sample	Reaction time in min	% *ortho*	% *meta*	% *para*	Total activity ($o + m + p$) in cts/mmol.s.
1.	10	2·3%	94·2%	3·5%	9·6
2.	20	3·5%	91·6%	4·9%	18·2
3.	30	5·3%	88·6%	6·1%	34·8
4.	45	7·4%	85·2%	7·4%	46·3
5.	60	9·3%	82·6%	8·1%	53·6
6.	90	13·7%	75·6%	10·7%	84·0
7.	180	24·0%	63·1%	12·7%	146·2

From these data and the composition of the equilibrium mixture: 37% *ortho*, 46% *meta* and 17% *para*, the following set of relative rate constants can be obtained:

$$k_{mo} = 1 \qquad k_{mp} = 1{\cdot}5 \qquad k_{op} = 6{\cdot}2$$
$$k_{om} = 1{\cdot}24 \qquad k_{pm} = 4{\cdot}0 \qquad k_{po} = 13{\cdot}0$$

These constants are in very good agreement with those found by Crump and Gornowicz.[6]

With the data of the Tables 1 and 2 and the results of activity measurements of "enriched" xylene mixtures (see Experimental) the Tables 4 and 5 are obtained.

TABLE 4. CALCULATED ACTIVITIES IN THE ISOMERIZATION OF *ortho*-BROMOTOLUENE. CONDITIONS AS IN TABLE 1.

Sample	Reaction time in min	*Ortho* act. in cts/mmol.s.	*Para* act. in cts/mmols.s.	Act. $o + m$ in cts/mmol.s.	Act. $p + m$ in cts/mmol.s.
1.	10	50	390?	48	260
2.	20	85	420	83	280
3.	30	110	400	100	260
4.	40	125	390	115	290
5.	50	140	370	135	270

TABLE 5. CALCULATED ACTIVITIES IN THE ISOMERIZATION OF *para*-BROMOTOLUENE. CONDITIONS AS IN TALBLE 2.

Sample	Reaction time in min	*Ortho* act. in cts/mmol.s.	*Para* act. in cts/mmol.s.	Act. $o + m$ in cts/mmol.s.	Act. $p + m$ in cts/mmol.s.
1.	5	440	32	240	30
2.	10	425	65	310	65
3.	15	405	108	300	102
4.	25	410	137	276	114
5.	30	360	181	265	163

DISCUSSION

The starting activity of the toluene used was 448 cts/mmol.s. Extrapolating the *ortho* activities of Table 4 to $t = 0$ (neglecting the first value), shows that the isomerization of *ortho* to *para*-bromotoluene is completely *inter*molecular. The activity of the *ortho* isomer indicates an *inter*molecular reaction *ortho* → *ortho*.

The activity of the *meta* isomer does not exceed that of the *ortho* isomer, hence the formation of *meta* from *ortho* is *intra*molecular in character. Comparison of the activation of the *ortho* and the *para* isomer yields

$$\frac{\%\,\textit{ortho} \times \text{act. }\textit{ortho}}{\%\,\textit{para} \times \text{act. }\textit{para}} = 1{\cdot}32 \text{ as mean value from Tables 1 and 4}$$

Similarly, it can be concluded from Table 5 that the *ortho* isomer is formed from the *para* isomer by an *inter*molecular reaction. The reaction *para* → *meta* is completely *intra*molecular. Also an activation of the *para* isomer occurs.

Comparison of the activation of the *ortho* isomer and the *para* isomer is as follows:

$$\frac{\%\ ortho \times \text{act. } ortho}{\%\ para \times \text{act. } para} = 1{\cdot}38 \text{ as mean value from tables 2 and 5}$$

From the experiments on catalytic bromination of alkylbenzenes,[8] under circumstances where no isomerization is possible, it can be extrapolated that for concentrations as low as used in experiments described in this paper, the *ortho*/*para*-ratio is about 1·3. This striking correspondence is in agreement with a complete *intra*-molecular *ortho* → *meta* and *para* → *meta* conversion.

Combination of this ratio with the relative reaction rates results in:

$$k_{oo} = 8 \quad \text{and} \quad k_{pp} = 10$$

From Table 3 it follows that in the *meta* isomerization the *ortho* and *para* isomers are formed in a ratio:

$$\frac{k_{mo}}{k_{mp}} = 0{\cdot}66$$

This means that the *meta* isomerizations do not take place via the same intermediate as the isomerizations of *ortho* and *para*-bromotoluene. If the radioactivity of the bromotoluene mixture from the isomerization of *meta*-bromotoluene is estimated for 100% *inter*molecular reaction, (the percentage of the *ortho* and the *para* component is simply multiplied by the activity of the toluene over the isomerization trajectory) and compared with the experimental data the following Table is obtained:

RADIOACTIVITY OF THE BROMOTOLUENE MIXTURE FROM *meta*-BROMOTOLUENE

Reaction time in min	Estimated for 100% *inter*molecular reaction cts/mmol.s.	Found cts/mmol.s.
10	25·8	9·6
20	36·8	18·2
30	51·1	34·8
45	63·2	46·3
60	73·0	53·6

From these data it is clear that the isomerization *meta* → *para* and *meta* → *ortho* is certainly not completely *inter*molecular. In comparable experiments samples were taken after 45 minutes at which time enough of the *ortho* component was present for separation and specific radioactive assay. The specific activity was found to be 94·5 resp. 101 cts/mmol.s. As only a small amount of the active *ortho* component was separated from a large amount of the nearly inactive *meta* component, these activities may well be higher. The activity of the *ortho* component should be at least about 100 cts/mmol.s. for a complete *intra*molecular isomerization (side reactions are neglected). In the case of a complete *inter*molecular reaction the activity should be 430 cts/mmol.s. Therefore it seems reasonable to assume a complete *intra*-molecular reaction *meta* → *ortho* and *meta* → *para*.

In the isomerization of *para*- and *ortho*-bromotoluene, the *ortho* and *para* isomers are formed in the same ratio independent of the starting isomer (1.3). In view of the agreement with Olah's experiments on catalytic bromination[8] it seems reasonable to assume that in the *inter*molecular isomerization a Br^+ is abstracted by the toluene in association with the catalyst, and then a new molecule of bromotoluene is formed. Therefore this transbromination probably takes place via the same intermediate as in the catalytic bromination. The *ortho* ⇄ *para* isomerizations are completely *inter*molecular and the *meta* ⇄ *para* and *meta* ⇄ *ortho* isomerizations proceed via 1,2-shifts. The mechanisms should be different.

meta-Isomerization proceeds presumably via σ-complexes, while *ortho* ⇄ *para* isomerization proceeds via a non-localized π-complex. (Olah assumed π-complexes for the catalytic bromination). The following scheme illustrates these conclusions:

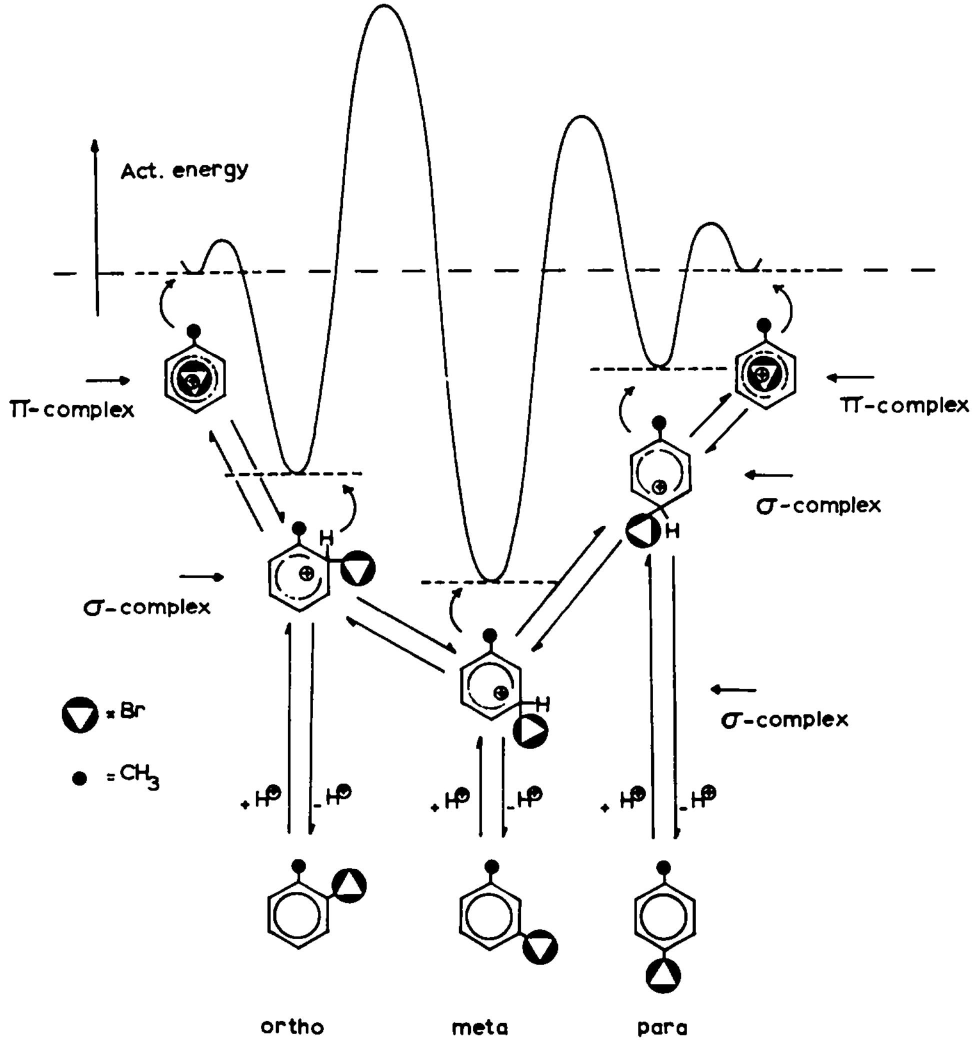

Fig. 1. Schematic representation of the isomerization of the bromotoluenes.

EXPERIMENTAL

Freshly sublimated Al_2Br_6 and freshly prepared HBr were used. The bromotoluenes were Fluka A.G. "isomerenfrei", the *ortho* and *para* isomer containing 3·4% *meta* isomer. Analar toluene was dried with CaH_2 and this toluene was activated with toluene-1-^{14}C (Philips–Duphar), to an activity of 448 cts/mmol.s.

For the isomerization ca. 750 mg (0·003 mole) Al_2Br_6 was sublimated in the reaction vessel and ca. 0·6 mole of radioactive toluene added. After saturation with HBr ca. 0·3 mole bromotoluene was added. Samples of 10 ml were taken and all manipulations carried out under strictly anhydrous conditions.

Samples were quenched with NaOH aq, neutralized and washed with water. The organic layer was separated in toluene and bromotoluenes by preparative GLC. (30% silicone oil on "Kieselguhr" column; length 2·4 m inner diam 6 mm, temp 140°, flow 150 ml H_2/min). The bromotoluenes were stripped with inactive toluene.

GLC analysis was performed in a two-stage-operation; *ortho*-analysis on a column of 20% dinonylphthalate on "Chromosorb", length 6 m, inner diam 6 mm, temp 110°, flow 100 ml H_2/min, retention time about 2 hr; *para*-analysis on a column of 33% tetrachlorodibutylphthalate on "Chromosorb", length 10 m, inner diam 4·5 mm, temp 110°, flow 120 ml H_2/min, retention time about 7 hr.

Radioactive assay of toluene-1-^{14}C and xylenes (see below) was carried out with a Packard 314 E S Tri Carb-liquid-scintillation spectrometer, quench corrections being applied for the bromotoluenes.

For the determination of the specific activity of each of the bromotoluenes it was necessary to convert these compounds into the corresponding xylenes (the Grignard reaction was used for this conversion). The preparative GLC separation was also carried out in a two-stage-operation; *ortho*-separation on a column of 30% silicone oil on "Kieselguhr", length 2·5 m, inner diam 6 mm, temp 100°, flow 60 ml H_2/min, separation of the *para* component on a Bentone 34 column (20% Bentone 34 + 2·5% silicone oil GE SF 80 on "Chromosorb"), length 4 m, inner diam 4·5 mm, temp 90°, flow 60 ml H_2/min.

The preparative GLC separation of xylenes was not complete. Therefore samples were enriched in the predominant isomer. The composition and the activity of the samples obtained was determined. By comparison with the composition and activity of the original xylene mixtures the activity of the *ortho* and *para* isomer was calculated.

A typical calculation example is given for the isomerization of *para*-bromotoluene, Table 2 No. 3.

Composition found 23·9% *ortho*, 10·1% *meta* and 66·0% *para*-bromotoluene, activity 174·6 cts/mmol.s.

This mixture was converted into xylenes; composition 23·0% *ortho*, 10·3% *meta* and 66·7% *para*-xylene, activity 171·9 cts/mmol.s.

Preparative GLC separation on the bentone column gave a mixture of 99·0% *para*-xylene and 1·0% *ortho* + *meta*-xylene, activity 110 cts/mmol.s. In the preparative GLC separation on the bentone column, the ratio *ortho*/*meta* remained practically unchanged.

The original mixture contained 33·3% (*ortho* + *meta*) and 66·7% *para* with an activity of 171·9 cts/mmol.s., the enriched mixture contained 1·0% (*ortho* + *meta*) and 99·0% *para*, with a total activity of 110 cts/mmol.s.

From the data, the following equations were derived:

$$0{\cdot}333\,(\text{act. O + M}) + 0{\cdot}67\,(\text{act. P}) = 171{\cdot}9$$
$$0{\cdot}01\,(\text{act. O + M}) + 0{\cdot}99\,(\text{act. P}) = 110$$

Hence act. O + M = 300 cts/mmol.s. and act. P = 108 cts/mmol.s.

In the preparative GLC separation on the silicone oil column the ratio *meta*/*para* remained practically unchanged.

The original mixture contained 77·0% (*meta* + *para*) and 23·0% *ortho* with an activity of 171·9 cts/mmol.s., the enriched mixture contained 98·8% (*meta* + *para*) and 1·2% *ortho*, with a total activity of 106 cts/mmol.s. This resulted in the following equations:

$$0{\cdot}77\,(\text{act. M + P}) + 0{\cdot}23\,(\text{act. O}) = 171{\cdot}9$$
$$0{\cdot}988\,(\text{act. M + P}) + 0{\cdot}012\,(\text{act. O}) = 106$$

Hence act. M + P = 102 cts/mmol.s. and act. O = 405 cts/mmol.s.

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