CATALYTIC ACTIVITY OF SYSTEMS LEWIS ACID–BROENSTED ACID IN DISPROPORTIONATION, ISOMERIZATION AND ALKYLATION REACTIONS

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Catalytic activity of $TiCl_4.RCOOH$ and $SnCl_4.2\ RCOOH$ complexes was tested in reactions of intermolecular alkyl transfer and of isomerization of aromatic hydrocarbons. In general, the activity of the catalysts decreased with the decreasing strength of aliphatic acids in an identical progression as found earlier in studies of H—D exchange. A higher acidity of the $TiCl_4.CF_3COOH$ complex in comparison with $TiCl_4.CCl_3COOH$ was confirmed by the intermolecular methyl group transfer which requires a stronger proton activation than the transfer of branched alkyls. However, both complexes are stronger catalysts than concentrated H_2SO_4. Both the activation of ortho- and para-positions of aromatic rings and preserving of the alkyl substituent structure in transfer and alkylation reactions show that they are — at the same time — gentler catalysts than $AlCl_3$, $AlBr_3$—H_2O, HCl or $HF.BF_3$. In the alkylation reactions halogen exchange between sec-butyl bromide and $TiCl_4$ complexes with acids (including H_2O) was observed simultaneously. In this way the existence of a complex between the complex acid and alkyl halides was verified in which a polarization of the C—X bond (necessary in alkylations) occurs.

Acidic properties of catalytic systems $TiCl_4$, $SnCl_4$–haloacetic acids $CH_{3-x}X_x$.
.$COOH$ $(X = Cl, F)$ or aliphatic acids have been characterized recently by measuring the H—D exchange rate of the complex acid proton with aromatic hydrocarbons[1]. The proton acidity of these catalysts is due to the acidic complexes $TiCl_4.RCOOH$ and $SnCl_4.2\ RCOOH$ whose existence was verified by infrared spectroscopy and by proton magnetic resonance[2]. In this communication, their acidic activity in disproportionation and isomerization reactions of aromatic hydrocarbons is demonstrated in the systems 1,2,4,5-tetramethylbenzene–m-xylene, di-tert-butylbenzene–benzene, and in pure 4-isopropyl-1-methylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene. Furthermore, the activity of the particular systems is compared in the alkylation of benzene by alkyl chlorides and bromides, and the influence of the component ratio of the catalytic systems as well as the effect of water on their activity is investigated. A comparison of the strength of the studied catalytic systems with the generally known Friedel–Crafts catalysts is made using the published data on the catalytic activity of the latter in the above mentioned reactions[3].

EXPERIMENTAL

Chemicals. TiCl$_4$ and SnCl$_4$ (Fluka) were re-distilled *in vacuo*. The acids CCl$_3$COOH, CHCl$_2$. .COOH (Koch and Light) and CHF$_2$COOH (Fluka) were distilled at a reduced pressure and first and last distillation fractions were removed. CF$_3$COOH and CH$_3$COOH were boiled with a small amount of anhydrides and the middle distillation fractions were used in the experiments. Benzene, toluene, and *m*-xylene were refluxed with LiAlH$_4$ for three hours and distilled using a column. 4-Isopropyl-1-methylbenzene was shaken 3-times with concentrated H$_2$SO$_4$, rinsed with water, dried by anhydrous Na$_2$CO$_3$ and fractionated. 1,3,5-Trimethylbenzene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene (Koch and Light) were used without any further purification. Tert-butyl chloride, sec-butyl chloride, sec-butyl bromide, n-butyl bromide, and isobutyl bromide were distilled before being used. The purity of all substances was checked by gas chromatography.

Tert-butylbenzene and di-tert-butylbenzene were prepared in alkylation of benzene by tert--butyl chloride in the following way: to the stirred mixture of tert-butyl chloride (46 ml), benzene (50 ml), and acetic acid (10 ml) stannic chloride was added (19 ml). The reaction mixture was kept at 50°C for 8-hours; during this time, evolution of hydrogen chloride was observed. The reaction mixture was then diluted by 50 ml of benzene, shaken several times with water, and the organic phase was dried by anhydrous Na$_2$CO$_3$. From the mixture benzene, tert-butylbenzene, and di-tert-butylbenzene were distilled and middle fractions of the latter were used. The di-tert-butylbenzene fraction contained, according to the gas chromatographic analysis, *para*- and *meta*-isomers in the ratio 18 : 1

Catalytic reactions. Catalytic systems were transferred into glass ampules with joints under the nitrogen atmosphere by means of syringes. The benzene solution (5M) of metal chloride was added as the last component in disproportionation and isomerization reactions; in alkylation reactions alkyl halide was the last component added. In the isomerization reaction of aromatic hydrocarbons, after the evolution of hydrogen chloride released in the catalyst formation[2] was completed, test-tubes were firmly closed and kept in polyethylene bags under nitrogen. During the alkylation the stopcocks were pressed by fine springs allowing for free release of hydrogen chloride overpressure. The reaction was stopped by mixing the reaction mixture with an excess of water. The organic phase was shaken out by water, dried by anhydrous Na$_2$CO$_3$, transferred into glass ampules and sealed off. The ampules opened only immediately before the chromatographic analysis.

The chromatographic analysis was carried out using a Chrom II apparatus, with a capillary column using squalane or silicon elastomer SE-33 as the stationary phase, and with the flame-ionization detector. In evaluating the results of disproportionation and isomerization reactions, the sum of all peak areas (corrected on the total number of carbons in the molecule) was taken as 100%. The analysis of di-tert-butylbenzene–benzene systems and the analysis of alkylation products in the system tert-butyl chloride–benzene was performed using calibration curves for di- and monotert-butylbenzene. Also, the determination of sec-butylchloride and sec-butyl-bromide concentrations in reaction mixtures was done by means of calibration curves.

The course of alkylations by tert-butyl chloride was also followed by means of proton magnetic resonance using a Tesla BS 487 80 MHz spectrometer. Infrared spectra of catalytic systems before and after alkylations were measured by a UR-10 Zeiss (Jena) instrument, as described earlier[2].

RESULTS AND DISCUSSION

Disproportionation and Isomerization of Aromatic Hydrocarbons

The acidic activity of a series of $TiCl_4$–RCOOH catalysts was tested at the room temperature using the transalkylation reaction of 1,2,4,5-tetramethylbenzene with *m*-xylene. The reaction product was mostly 1,2,4-trimethylbenzene. The results are shown in Table I. The most active system $TiCl_4$—CF_3COOH was used under mild conditions (35°C, 12 days) to study the hydrocarbon transformation in the system 1,3,5-trimethylbenzene–toluene and 1,2,4-trimethylbenzene–toluene (component ratio 1 : 3 in both cases). In the former case 4% of the mixture of *m*- and *p*-xylenes and 2% of 1,2,4-trimethylbenzene, in the latter case 6% of *m*- and *p*-xylenes and 8% of *o*-xylene and practically no 1,3,5-trimethylbenzene was formed. As under given experimental conditions a reliable separation of *m*- and *p*-xylenes could not be performed, we report here on the mixture of both. Pure 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene gave with the same catalyst at the room temperature during 16 days of the reaction time the following main products: 1,3,5-trimethylbenzene: 1,2,3,5-tetramethylbenzene 5%, 1,2,3-trimethylbenzene 0·6%, *m*- and *p*-xylene 4%, toluene 0·4%; 1,2,4-trimethylbenzene: 1,2,4,5-tetramethylbenzene 19%, 1,2,3-trimethylbenzene 0·3%, 1,3,5-trimethylbenzene 1%, *o*-xylene 6%, *m*- and *p*-xylene 11%, toluene 0·3%. With 1,3,5-trimethylbenzene one may assume that the mixture of xylenes consists mostly of *m*-xylene, with 1,2,4-trimethylbenzene one may expect mostly *p*-xylene in view of the high *o*-xylene content.

TABLE I

Disproportionation in the System *m*-Xylene–1,2,4,5-Tetramethylbenzene Induced by Catalysts $TiCl_4$–RCOOH

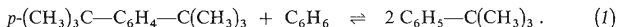Experimental conditions: 3 mmol $TiCl_4$, 3 mmol RCOOH, 3·7 mmol 1,2,4,5-tetramethylbenzene, 12 mmol *m*-xylene, temperature 20—23°C, 21 days. Amount of products in percent of the initial amount of 1,2,4,5-tetramethylbenzene.

Acid	1,2,4-Trimethyl	Acid	Benzene, %
CF_3COOH	10·1[a]	$CH_2ClCOOH$	0·7
CCl_3COOH	1·4	CH_3COOH	0·6
$CHCl_2COOH$	1·0	H_2SO_4	5·2 [b]

[a] In addition in the system was formed 1·0% toluene, 1·0% 1,3,5-trimethylbenzene, 1·0% 1,2,3-trimethylbenzene, 0·1% 1,2,3,5-tetramethylbenzene, 0·3% 1,2,3,4-tetramethylbenzene; [b] in the heterogeneous system with 0·2 ml 98% H_2SO_4 was formed in addition 0·1% 1,3,5-trimethylbenzene and 1·0% toluene.

The activity of a large series of catalysts was tested on the isomerization of 4-iso-propyl-1-methylbenzene (Table II). Main products of the action of the catalysts on 4-isopropyl-1-methylbenzene are (besides 3-isopropyl-1-methylbenzene) toluene and a mixture of di-isopropylmethylbenzenes. In the action of the strongest catalysts the following substances were found in amounts smaller by an order of magnitude: xylenes, isopropylbenzene, 2-isopropyl-1-methylbenzene, and methyl derivatives of isopropylmethylbenzenes. The presence of 4 chromatographic peaks of the C_{13} fraction, whose relative intensities change with the catalyst used, show that the isomerization of the di-isopropyltoluenes formed occurs easier than the isomerization of 4-isopropyl-1-methylbenzene. In all the reported reactions catalysts $SnCl_4$—RCOOH were tested, too, but they proved themselves to be entirely non-reactive.

A comparison of the acidic activity of strong and weak catalysts was made possible by studying the tert-butyl transfer in the reaction

$$p\text{-}(CH_3)_3C\text{—}C_6H_4\text{—}C(CH_3)_3 + C_6H_6 \rightleftharpoons 2 C_6H_5\text{—}C(CH_3)_3 . \qquad (1)$$

The course of the tert-butyl transfer was practically identical with CF_3COOH—$TiCl_4$ and CCl_3COOH—$TiCl_4$, and it is shown in Fig. 1. The reaction was carried out

TABLE II

Products of Action of $TiCl_4$—RCOOH Catalysts on 4-Isopropyl-1-methylbenzene

Experimental conditions: 3 mmol $TiCl_4$, 3 mmol RCOOH, 9·5 mmol 4-isopropyl-1-methyl-benzene, temperature 35°C, 13 days. Amount of products in percent of the initial amount of 4-iso-propyl-1-methylbenzene; C_7 toluene, C_9 isopropylbenzene, C_{13} sum of diisopropylmethylbenze-nes.

Acid	C_7, %	C_9, %	3-Isopropyl-1-methylbenzene	C_{13}, %
CF_3COOH	13·5	0·7	6·7	11·5
CCl_3COOH	7·0	0·1	0·6	5·6
CHF_2COOH	4·9	0·1	1·4	4·5
$CHCl_2COOH$	6·0	0·1	0·8	4·2
$CH_2ClCOOH$	1·2	—	0·2	0·2
CH_3COOH^a	1·5	—	1·1	—
CF_3COOH^b	0·3	—	0·1	—
$TiCl_4^b$	0·3	—	—	—

^{a} A small amount of acetyl chloride is formed in the system by the reaction $TiCl_4 + RCOOH = TiCl_3OH + RCOCl$, products of isopropylmethylbenzene acetylation found among the products; ^{b} without the second component of the catalyst.

in an considerable excess of benzene and, therefore, its course was practically pseudo-unimolecular. p-Di-tert-butylbenzene contained always 5·5% of m-di-tert-butylbenzene whose concentration did not change during the experiment (Fig. 1). This shows its considerable inertness towards acidic catalysts. The value of the reciprocal equilibrium constant of reaction (1), $K \approx 0·5$, agrees qualitatively with the equilibrium constant[4] of the same reaction of ethyl derivatives, $K \approx 0·2$, catalyzed by the stronger acid HF—BF₃. Conversions of di-tert-butylbenzene by strong and weak catalysts during 5 days are shown in Table III.

It follows from the results of the disproportionation and isomerization reactions of aromatic hydrocarbons that the TiCl₄—RCOOH catalysts belong to the Friedel–Crafts catalysts of an activity comparable e.g. with sulphuric acid or hydrogen fluoride acid[5], while the systems SnCl₄–acids are considerably weaker than the above mentioned Friedel–Crafts catalysts. The example of polymethylbenzenes showed that the effect of the catalysts used did not lead to the formation of the most basic aromatic hydrocarbons, but that the methyls transferred were directed towards ortho- and para-positions. On the other hand, methylbenzenes with alkyl substituents in ortho- and para-positions were more activated and formed more intermolecular transalkylation products than more basic aromatic compounds with alkyls in meta-positions (e.g., 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene). The high fraction of intermolecular transfer of methyls, exceeding their intramolecular migration (isomerization), is rather surprising. The alkyl transfer between aromatic compounds is the easier the more stable is the transferred alkyl cation; the transalkylation rate increases in the series methyl < isopropyl < tert-butyl (Table I, II, III). Also, the reactivity of aromatic compounds is proportional to their basicity, which increases with the alkyl-substituent number and depends on their mutual position (see the results of methylbenzene transformations). However, the structure of alkylsubstituents has but a negligible effect due to the compensation of the induction effect
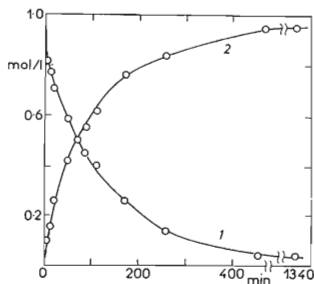

FIG. 1

Course of Reaction Di-tert-butylbenzene + + Benzene ⇌ Tert-butylbenzene Catalyzed by TiCl₄—CF₃COOH System

1 Concentration of tert-butyl groups in the form of p-ditert-butylbenzene, 2 concentration of tert-butylbenzene; reaction conditions: 0·5 mol/l solution of di-tert-butylbenzene in benzene, 6 mmol TiCl₄, 6 mmol CF₃. .COOH, temperature 22°C.

by the hyperconjugation, and thus the basicity of tert-butyl and methyl derivatives was found to be practically the same[6].

The intramolecular isomerization migration is typical for strong Friedel–Crafts catalysts, e.g., HF—BF$_3$ (ref.[4,5,7]), AlCl$_3$, and AlBr$_3$ (ref.[8]), which form strong complexes with aromatic hydrocarbons. In these complexes an easy intramolecular isomerization of the aromatic hydrocarbon occurs to the most basic isomer (positions 1,3- 1,3,5- 1,2,3,5) forming a stronger complex with the catalyst[8,9]. The intramolecular isomerization is initiated also by protonic catalysts, used in this study, e.g., in the isomerizations 4-isopropyl-1-methylbenzene → 3-isopropyl-1-methylbenzene, 1,2,4-trimethylbenzene → 1,3,5-trimethylbenzene. However, the rate of this isomerization was always smaller than the rate of the intermolecular transalkylation. In the case of tert-butylbenzenes the isomerization rate was entirely negligible in comparison with the transalkylation rate.

The mechanism of isomerization assumes the 1,2 — shift of alkyls on the protonated aromatic ring (I). The intermolecular alkyl transfer occurs in a substitution reaction which is made possible by the protonization of the aromatic hydrocarbon and by the stability of the liberated cation R$^{(+)}$. The transfer of alkyl R$^{(+)}$ occurs with the aid of a second aromatic molecule in the complex (II), because no products with isomerized alkyls were found among the reaction products and no isobutylene oligomers (products of reactions of free cations[7,10] were formed in di-tert-butylbenzene.

I

II
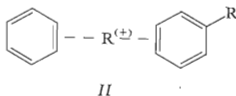
The results of the transalkylation and isomerization reactions of aromatic hydrocarbons in all the systems studied show that the catalytic activity of the systems TiCl$_4$—RCOOH (1 : 1) in dependence on the type of the haloacetic acid used follows the same trend as their activity in the electrophilic D—H substitution reaction[1]. The rates of both substitution reactions, whose first step is a partial protonization of the aromatic ring, are the higher the stronger is the aliphatic acid and they increase in the series CH$_3$COOH < (CH$_2$ClCOOH < CHCl$_2$COOH < CHF$_2$COOH < < CCl$_3$COOH < CF$_3$COOH. The differences in the acidity of the complexes TiCl$_4$.RCOOH in this series are even higher. This is because in the reaction system (2)

$$RCOOTiCl_3 + HCl \rightleftharpoons RCOOH + TiCl_4 \rightleftharpoons TiCl_4.RCOOH \qquad (2)$$

the higher amount of inactive titanium carboxylate is formed, the stronger acid is

used, and also the equilibrium of the complex formation shifts considerably towards the initial components. In the system with CH_3COOH the equilibrium in equation (2) is shifted entirely towards the complex formation, in the system with CF_3COOH only by several percent[2].

The results on the reaction of tert-butyl transfer with $SnCl_4$–RCOOH confirm the activity series observed earlier in H—D exchange reactions: $CH_3COOH >$ $> (CH_3)_3COOH > CF_3COOH$ (ref.[1]). The activity series in the former two systems differs from that one observed in H—T exchange reaction with aromatic hydrocarbons[11].

Alkylation of Benzene by Tert-butyl chloride

The course of alkylation of benzene by tert-butylchloride catalyzed by $TiCl_4$— —RCOOH (1 : 1) and by $TiCl_4$—H_2O was followed by PMR spectroscopy (Fig. 2). The series of catalyst activity was found to be the same as in the disproportionation and isomerization reactions. The only exception was $TiCl_4$—CF_3COOH which showed about the same activity as the system $TiCl_4$—CCl_3COOH, similarly as in the H—D exchange and the tert-butyl transfer reaction. It can be seen from Fig. 2 that an equimolar addition of water to $TiCl_4$ increases the activity of the system, as it was described earlier in the alkylation reactions[3,12]; however, the activity of this catalyst is not as high as that one of $TiCl_4$—$CH_2ClCOOH$. A thorough drying of all components of the system results in a decreased catalytic activity of $TiCl_4$. Therefore,

TABLE III

Alkyl Transfer in the Reaction Di-tert-butylbenzene + Benzene ⇌ Tert-butylbenzene Catalyzed by $TiCl_4$, $SnCl_4$—RCOOH

Experimental conditions: 3 mmol $TiCl_4$ (or $XnCl_4$), RCOOH:$TiCl_4$ = 1, RCOOH:$SnCl_4$ = 2, 6 mmol CF_3COOH, 4 ml 0·5 mol/l solution of di-tert-butylbenzene in benzene, temperature 22°C, 5 days.

Catalyst	Conversion to tert-butylbenzene %
$TiCl_4$—CF_3COOH	95
$TiCl_4$—CCl_3COOH	95
$TiCl_4$—CH_3COOH	44
$SnCl_4$—CH_3COOH	10
$SnCl_4$—$(CH_3)_3CCOOH$	2
$SnCl_4$—CF_3COOH	0
CF_3COOH	0

it may be assumed that non-protonic activation of the alkylation by $TiCl_4$ is a rather ineffective process, if it occurs at all. An addition of water to the most effective catalyst, $TiCl_4$—CF_3COOH, in the ratio Ti : RCOOH : H_2O = 1 : 1 : 1 does not change its activity.

A detailed chromatographic analysis of products during the alkylation with the system $TiCl_4$—CF_3COOH showed that in the initial phases of the reaction besides tert-butylbenzene also a large amount of di-tert-butylbenzene was formed, which changed to tert-butylbenzene in a subsequent reaction (Fig. 3). The alkylation of tert-butylbenzene is faster than that of benzene; this is evident in particular at the beginning of the reaction, when the tert-butylbenzene concentration is much smaller than that of benzene. It is the consequence of a higher basicity of tert-butylbenzene, as the logarithm of the rate constant of both H—D and alkylation reaction (occurring pseudounimolecularly[1,13] in an excess of an aromatic hydrocarbon) is approximately linearly proportional to the aromatic hydrocarbon basicity[14].

In Table IV the results of testing several systems $TiCl_4$—RCOOH are given for various ratios of both catalyst components. In all instances the catalysts with the component ratio 2 : 1 exhibit a higher activity than those with the ratio 1 : 1. This is
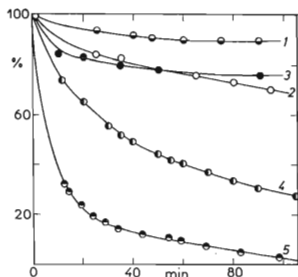
FIG. 2

Conversion of Tert-butyl-chloride in Alkylation of Benzene Catalysed by Catalytic Systems

1 $TiCl_4$, *2* $TiCl_4$-$CH_2ClCOOH$, *3* $TiCl_4$/H_2O = 1, *4* $TiCl_4$-$CHCl_2COOH$, *5* $TiCl_4$-CCl_3COOH (conversion identical with $TiCl_4$-CF_3COOH); reaction conditions: 1 mmol tert-butyl chloride, 1 mmol $TiCl_4$, 1 mmol RCOOH, 32 mmol benzene, temperature 22°C.
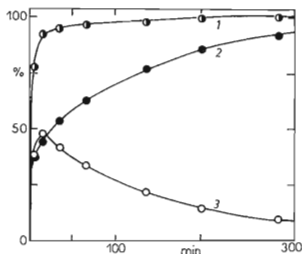
FIG. 3

Kinetics of Product Formation in Alkylation of Benzene by Tert-butyl Chloride

2 Concentration of tert-butyl groups in the form of tert-butylbenzene, *3* di-tert-butylbenzene, *1* both compounds; reaction conditions: 1 mol/l solution of tert-butyl chloride in benzene (10 ml), 7 mmol $TiCl_4$, 7 mmol CF_3COOH, temperature 22°C.

caused both by a higher concentration of the complex in the systems containing strong acids and by the solvation of the complexes formed by $TiCl_4$ which increases their acidity[2]. Table IV shows also the composition of the products tert-butylbenzene : di-tert-butylbenzene and p-ditert-butylbenzene : m-di-tert-butylbenzene, changing during the alkylation process. With the increasing strength of the aliphatic acid used and with the increasing reaction time the fraction of tert-butylbenzene with respect to di-tert-butylbenzene increases. It follows from the table, too, that in the transalkylation reaction the *para*-isomer takes part, as the ratio *para* : *meta* decreases with the increasing ratio mono-: di-derivative. When comparing the amount of products obtained with the catalyst of the same component ratio, the activity series of $TiCl_4$ systems is $CCl_3COOH > CH_2ClCOOH > CH_3COOH$. Pure $TiCl_4$ under the same conditions appears to be a weak catalyst of an activity comparable to that one of $TiCl_4$—CH_3COOH (1 : 1). With the increasing concentration of $TiCl_4$ the degree of alkylation increases, however, during the reaction the ratio mono--derivative : di-derivative decreases; this shows that the complex acid composed of $TiCl_4$ and water traces practically does not catalyse the disproportionation reaction (1). Catalytic systems $SnCl_4$–aliphatic acids bring about a very slow alkylation by tert-butyl chloride at the laboratory temperature. Following the course of the reaction was very difficult here, as a reasonable alkylation rate could be achieved

TABLE IV
Influence of $TiCl_4$ Concentration and Component Ratio of the Systems $TiCl_4$—RCOOH on the Course of Alkylation of Benzene by Tert-butyl Chloride and on the Product Composition

Experimental conditions: 1 mmol RCOOH, 3 mmol tert-butyl chloride, 15 mmol benzene, 0·5, 1·0, and 2·0 mmol $TiCl_4$; samples taken after 2, 4, and 20 hours.

RCOOH	$TiCl_4$	Alkylation degree, %			Mono-: di-tert--butylbenzene			para : meta
1 mmol	mmol	2 h	4 h	20 h	2 h	4 h	20 h	20 h
CCl_3COOH	0·5	21	32	75	0·6	0·7	1·2	9·5
	1·0	28	46	82	0·7	1·1	3·5	1·3
	2·0	34	62	100	0·9	2·1	7·4	0·7
$CH_2ClCOOH$	1·0	22	42	61	0·7	1·0	1·2	9·2
	2·0	29	52	94	1·1	1·1	1·7	4·4
CH_3COOH	1·0	—	10	58	—	9·6	0·7	15·0
O	2·0	24	43	72	0·8	0·8	1·1	6·7
O	0·5	10	14	37	1·6	1·5	1·2	9·9
O	1·0	12	16	51	2·7	1·3	0·7	10·8
O	2·0	13	18	62	3·6	0·8	0·6	14·5

only by heating the system to 40°C (see Experimental), and at a certain alkylation stage two liquid phases were formed.

Alkylation of Benzene by Sec-butyl Chloride and Sec-butyl Bromide

The alkylation by sec-butyl halides is substantially slower than that one by tert-butyl chloride and the alkylation by n-butyl halides does not occur at all. Products of this alkylation are sec-butylbenzene and a mixture of di-sec-butylbenzenes. The chromatographic analysis of the decrease of sec-butyl chloride concentration showed a much higher activity of complex systems with haloacetic acids than of $TiCl_4$ alone (with H_2O) (Fig. 4). It can be also seen from Fig. 4 that the conversion of sec-butyl bromide is unexpectedly slower than the conversion of sec-butyl chloride and that the alkylation by sec-butyl bromide is always accompanied by the conversion of sec-butyl bromide to sec-butyl chloride. Vertical lines in Fig. 4 and Fig. 5 indicate the percentage of conversion of sec-butyl bromide to sec-butyl chloride. The catalysts with the double excess of $TiCl_4$ are more active than the 1 : 1 catalysts both in the halogen exchange and alkylation reaction (Fig. 4 and Fig. 5). The conversions in Fig. 5 give the activity series of the catalysts according to the aliphatic acid strength in agreement with the earlier findings. The halogen exchange reaction, similarly as the alkylation process, does not proceed in the n-butylbromide system.

The reaction of halogen exchange occurs between $TiCl_4$ and sec-butyl bromide; the halogens of haloacetic acids do not take part in it, as it occurs in the system with $TiCl_4$ only or in the system $TiCl_4$—CH_3COOH. Also, infrared spectra of the reacting systems do not give any evidence concerning the conversion of chlorinated acids to bromoderivatives. The halogen exchange process is evidently faster than the alkylation process, as strong catalysts bring about a fast increase of the chloride centration followed by its decrease due to the alkylation reaction, while in the systems with weak alkylation catalysts sec-butyl chloride accumulates during the reaction. A lower conversion in the alkylations by sec-butyl bromide in comparison with those by sec-butyl chloride are evidently caused by a lower activity of the catalyst in which the conversion of $TiCl_4$ to $TiCl_{4-x}Br_x$ and, finally, to $TiBr_4$ occurs. As the acidity of halides of the metals of the fourth group, MX_4, with respect to the oxygen-containing bases strongly decreases in the series Cl > Br > I (ref.[15]), it may be assumed that complexes of acids with titanium bromides will exhibit a substantially lower acidity than the original complexes with $TiCl_4$.

The halogen exchange can proceed only in the intermediate complex containing $TiCl_4$ and sec-butyl bromide, as the exchange HCl–sec-butyl bromide under the same conditions does not occur. As the halogen exchange is fastest in complexes with haloacetic acids, one may assume that $TiCl_4$ bound in the complex with the acid takes part in the exchange. Weakening of the Ti—Cl bonds by the fifth-ligand (acid)

coordination is not a sufficient condition for the exchange: in the complex $TiCl_4$—
—CH_3COOH, where the strong $Ti—O=C(OH)CH_3$ bond causes the strongest
weakening of the $Ti—Cl$ bonds, the exchange occurs at a lower rate than in the
systems with haloacetic acids, whose complexes with $TiCl_4$ exhibit a much weaker
coordination bond to oxygen[2]. A very slow exchange of halogens with pure $TiCl_4$
can be explained by the co-catalysis of water traces in an imperfectly dried system.

Investigation of the alkylation reaction by means of the infrared spectroscopy
method proved both the conversion of sec-butyl bromide (absorption at 533 cm^{-1}
(m), 1160 cm^{-1} (s), and 1240 cm^{-1} (s)), and the loss of $TiCl_4$ (absorption at 495
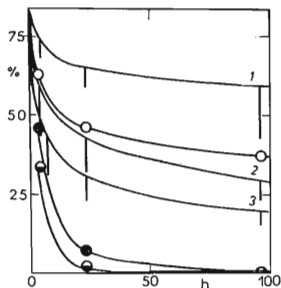cm^{-1} (vs)). At the same time, small changes, difficult to interpret, were observed

Fig. 4

Comparison of Activities of Catalysts $TiCl_4$—RCOOH (1 : 1) in Alkylation of Benzene by Sec-butyl Chloride and Sec-butyl Bromide

Conversion of sec-butyl chloride to sec-butylbenzenes denoted by points: ○ catalyst $TiCl_4$, ● catalyst $TiCl_4–CHCl_2COOH$, ◐ catalyst $TiCl_4–CCl_3COOH$. Conversion of sec-butyl bromide to sec-butylbenzenes is given by the upper end of vertical line, the length of the vertical line gives the amount of sec-butyl chloride formed in exchange between sec-butyl bromide and $TiCl_4$: 1 catalyst $TiCl_4$, 2 catalyst $TiCl_4–CHCl_2COOH$, 3 catalyst $TiCl_4–CCl_3COOH$. Reaction conditions: 1 mmol $TiCl_4$, 1 mmol RCOOH, 3 mmol sec-butyl halide, 15 mmol benzene, temperature 22°C; chromatographic analysis using calibration curves.
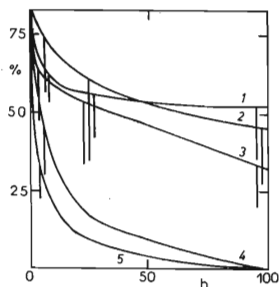
Fig. 5

Comparison of Activities of Catalysts $TiCl_4$–RCOOH (2 : 1) in Alkylation of Benzene by Sec-butyl Bromide and in Halogene Exchange between Sec-butyl Bromide and $TiCl_4$

Upper end of vertical line gives conversion of sec-butyl bromide to alkylaromatic compounds, the length of the line conversion to sec-butyl chloride: 1 catalyst $TiCl_4$, 2 catalyst $TiCl_4–CH_3COOH$, 3 catalyst $TiCl_4–CH_2ClCOOH$, 4 catalyst $TiCl_4–CHCl_2$.COOH, 5 catalyst $TiCl_4–CCl_3COOH$. Reaction conditions: 2 mmol $TiCl_4$, 1 mmol RCOOH, remaining same as in Fig. 4.

in the relative intensities of absorption bands of ν(C=O)vibrations of titanium carboxylate and $TiCl_4$–acid complexes[2]. The decrease of free $TiCl_4$ absorption corresponds to the gradual exchange of chlorine for bromine; this leads to a decrease of absorption wavenumbers down to the unmeasured region bellow $400\ cm^{-1}$. Bands occurring at about $450\ cm^{-1}$ and appearing only in certain phases of the reaction process belong presumably to mixed halides $TiCl_{4-x}Br_x$ (ref.[16]). For comparison, infrared spectra of the same systems with n-butyl bromide, measured during the time interval of serveral days, did not show any change. A decrease of $TiCl_4$ absorption as well as the other (accompanying) changes were observed when benzene solutions of $TiCl_4$—RCOOH catalysts were saturated by gaseous hydrogen bromide; this confirms the occurrence of HBr—$TiCl_4$ exchange.

Even though it was shown in this way that hydrogen bromide released in alkylation reaction (3)

$$C_4H_9Br\ +\ C_6H_6\ \rightarrow\ C_6H_5C_4H_9\ +\ HBr \qquad (3)$$

exchanges with chlorine of $TiCl_4$, it can be hardly assumed that hydrogen chloride thus introduced into the system or released during the catalyst formation (equation (2)) exchanges with RBr to form RCl. The polarization of hydrogen chloride in the presence of $TiCl_4$ is negligible, as HCl does not have any catalytic activity even in tert--butyl alkylations in the presence of $TiCl_4$.

The influence of the proton in the $TiCl_4$—RCOOH complex on the alkyl halide, leading to the $C_4H_9^+$ cation formation and to the halogen exchange, is presumably of prime importance in determining the halogen-exchange rate and the alkylation rate. As the co-catalytic influence of RCOOH acids was proved in both reactions, the intermediate complex in the two reactions is of the type III rather than IV.

III   *IV*
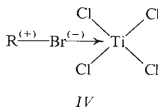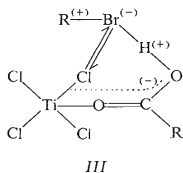
The exchange of titanium chlorine with hydrogen bromide occurs probably in complex *III*, where RBr is substituted by HBr. The alkylation occurs by R^+ addition to the aromatic ring followed by H^+ elimination, rather than by the effect of protonated aromatic ring on alkyl halide.

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Translated by Z. Herman.