THE MECHANISM OF ALKYLATION OF BENZENE WITH CARBOXYLIC ACID ESTERS INDUCED BY TITANIUM TETRACHLORIDE
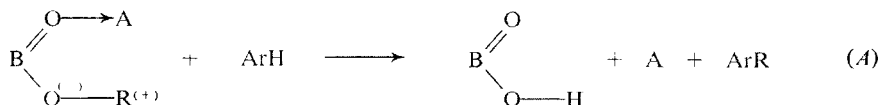
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The alkylation of benzene by secondary and tertiary alkyl esters of carboxylic acids in the presence of titanium tetrachloride proceeds through the formation of intermediate alkyl chlorides. Both the decomposition of esters and the alkylation with the respective alkyl chlorides is catalysed by strongly acidic complexes $RCOOH.TiCl_4$ formed in the autocatalytic reaction during the ester decomposition.

Olah and Nishimura[1] have recently investigated alkylations of benzene and toluene by alkyl chlorosulfites, arenesulfinates, tosylates, chloro- and fluorosulfates, trifluoromethanesulfonates, and trifluoroacetates catalysed by strong Lewis acids, *e.g.* $AlCl_3$ and SbF_5. They found that the alkylation reaction proceeded the easier the stronger was the parent acid of the ester, the more basic was the alkyl of the ester, and the stronger Lewis acid was used to catalyse the reaction. The catalytic effects of Lewis acid has been assumed[1,2] to lie in the formation of a complex with the ester leading to the alkyl–oxygen bond cleavage followed by the alkylation of aromatic hydrocarbons and the free acid evolution according to Eq. (*A*) where BOOR is the ester of strong acid

$$
\begin{matrix}
O \longrightarrow A \\
B \diagup \diagdown \\
\diagdown O \underline{\quad} R^{(+)}
\end{matrix}
\quad + \quad ArH \quad \longrightarrow \quad
\begin{matrix}
O \\
B \diagup \diagdown \\
\diagdown O \underline{\quad} H
\end{matrix}
\quad + \quad A \quad + \quad ArR \qquad (A)
$$

This paper describes the titanium tetrachloride-catalysed alkylation of benzene with secondary and tertiary alkyl esters of relatively weak acetic and haloacetic acids and the mechanism of alkylation as studied by PMR and IR spectroscopy.

EXPERIMENTAL

Isopropyl, sec-butyl and tert-butyl esters of acetic acid, mono-, di- and trichloro- and fluoro-acetic acids were prepared by boiling the respective alcohols with acids. After washing with water and short drying with anhydrous sodium carbonate the product was fractionated. Tert-butyl esters of trichloro- and trifluoroacetic acids were prepared by the addition of isobutylene to the

acids as described earlier[3] and fractionated at the pressure of 20 Torr. The purity of esters was checked by gas chromatography. Titanium tetrachloride was fractionated and distributed into ampoules on a vacuum line. Its solutions in benzene were prepared on the vacuum line, too, using benzene dried by $LiAlH_4$. Solutions of esters were mixed with $TiCl_4$ solutions under nitrogen atmosphere using the syringe technique. The same technique was used also for filling infrared (KBr) cells and ^{1}H-NMR tubes. ^{1}H-NMR spectra of reacting systems after short mixing in ^{1}H-NMR tubes were measured at 25°C. Concentrations of esters for infrared measurements were 0·1 mol/l, those for ^{1}H-NMR measurements 2 mol/l.

Infrared spectra were measured on a UR-10 (Zeiss, Jena) infrared spectrometer. ^{1}H-NMR spectra were obtained using a Tesla 487 proton magnetic resonance spectrometer at 80 MHz. The analyses of final alkylation mixtures, after washing them with excess water and drying with soda, were carried out on a Chrom II gas chromatograph using a capillary column with squalane or silicone as a stationary phase.

RESULTS AND DISCUSSION

While studying the interactions between $TiCl_4$ and carboxylic acid esters we confirmed the earlier observation[4] that the complexes of isopropyl, sec-butyl and tert-butyl esters decomposed after some time, while those of n-alkyl esters were stable[5]. The benzene solutions of sec-alkyl ester complexes turned orange-red at room temperature after an induction period, and hydrogen chloride evolution was observed. The decomposition of tert-butyl ester complexes was so fast that the complex formation could be detected in the infrared spectrum only during the initial 5 minutes after mixing the components and only in the case of the least reactive tert-butyl acetate. Complexes of $TiCl_4$ with some esters of acetic and haloacetic acids, mainly of the 1 : 1 composition, were characterised by the decrease of the ester $\nu(C{=}O)$ frequency due to the complex formation, $\Delta\nu(C{=}O)$, and by equilibrium constants of the complex formation K. Both values are given in Table I. They show that the strength of the electron–donor bond in the complexes decreases with the increasing halogen substitution in acyl, but increases slightly with the degree of branching on the α-carbon atom of the ester alkyl.

The course of the reactions proceeding in the systems isopropyl and sec-butyl acetates–$TiCl_4$–benzene could be followed by ^{1}H-NMR. After an induction period (see Fig. 1 and Table I) a fast decomposition of the esters was observed leading to the formation of sec-alkyl chloride. Somewhat later the alkylation of benzene started in addition to the continuing ester decomposition. A typical time dependence of the concentrations of sec-butyl trifluoroacetate, sec-butyl chloride and sec-butylbenzene is shown in Fig. 1. After the complete disappearance of the ester, the alkylation of benzene with sec-butyl chloride proceeded until completion. The addition of sec--butyl chloride to the reaction mixture, after all ester and sec-butyl chloride had been consumed, brought about a further alkylation with the reaction rate similar to that observed with sec-butyl chloride generated by ester decomposition. The initial induction period disappeared upon addition of small amount of carboxylic acid,

TABLE I

Characteristics of $TiCl_4$–R'COOR Systems
Values of the induction period and k are given for the systems at the components ratio 1 : 1.

R'	R	$\Delta\nu(C=O)$ cm^{-1}	K^a	Induction period, min	k^b %/min
CF_3	sec-C_4	51	0·07	11	5·7
CF_3	iso-C_3	52	—	27	2·2
CCl_3	sec-C_4	60	0·2	5	20·0
CCl_3	iso-C_3	—	—	25	6·6
CHF_2	sec-C_4	73	0·9	—	—
$CHCl_2$	sec-C_4	83	1·8	16	13·3
				15	6·6^c
				60	0·5^d
$CHCl_2$	n-C_4	79	1·5	stable	—
CH_2F	sec-C_4	110	60	days	—
CH_2Cl	sec-C_4	110	80	days	—
CH_2Cl	n-C_4	106	37	stable	—
CH_3	sec-C_4	118	17 000	stable	—
CH_3	n-C_4	112	1 200	stable	—

^{a} Equilibrium constant of the reaction R'COOR $+$ $TiCl_4$ $\rightleftharpoons$ R'COOR.$TiCl_4$ obtained by infrared analyses of R'COOR concentration on mixing the ester with $TiCl_4$ in benzene solution; infrared spectra were taken during the induction period. ^{b} Rate of the ester decomposition between 60 and 40% of the initial amount of ester (maximum rate, see Fig. 1). ^{c} Molar ratio $TiCl_4$/ester $=$ $=$ 2. ^{d} Molar ratio $TiCl_4$/ester $=$ 0·5.
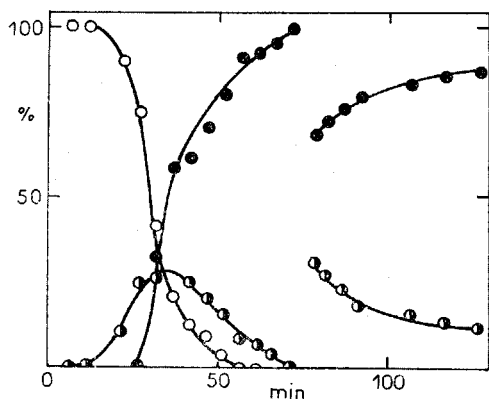

FIG. 1

The Course of the Reaction of Sec-butyl Trifluoroacetate (1 mmol) $+$ $TiCl_4$ (1 mmol $+$ $+$ Benzene (0·5 cm^3) Followed by PMR Spectra

○ Concentration of the ester; ◑ concentration of sec-butyl chloride; ● concentration of sec-butylbenzene. In the 74 minute of the reaction 0·5 mmol of sec-butyl chloride was added. All concentrations in mol.%.

while bubbling HCl into the $TiCl_4$-ester solution had no effect. Also the addition of a little amount of water (less then 0·5 mmol) to the ester before addition of $TiCl_4$ did not influence observably the induction period. The ratio $TiCl_4$: ester influences all the reactions proceeding in the system. At a ratio below the optimum value 1, the induction period is extended and the maximum decomposition rate of ester k decreases (Table I). At a ratio above the optimum value, the induction period is not affected, but the rate of alkylation is increased and consequently, lower intermediate concentrations of sec-alkyl chloride are observed. The decomposition and the alkylation reactions were much faster if tert-butyl esters were used. Only products of a complete alkylation of benzene were observed in ^{1}H-NPMR spectra after 3 minutes of reaction, except in the case of tert-butyl acetate, where a fast alkylation reaction by tert-butyl chloride generated in the system could be followed.

Infrared spectra of reacting isopropyl and sec-butyl ester systems revealed that the titanium trichloride carboxylate and hydrogen chloride, characterised by their $v(C=O)$ and $v(H-Cl)$ ($2750 \, cm^{-1}$) vibration bands[6], respectively, were formed in the early stage of the ester decomposition reaction. In the course of the reaction the band of the $v(C=O)$ vibration of the complex $RCOOH.TiCl_4$ appeared to grow, too, in addition to the growing band of the carboxylate up to the point where all the free and $TiCl_4$-complexed ester disappeared. Some amount of the free carboxylic acid (monomer and dimer) was observed in the infrared spectra at the end of the reaction. The region of the $v(C=O)$ vibrations of the infrared spectra in the sec-butyl dichloroacetate–$TiCl_4$–benzene system, prior to and after the decomposition reaction, is shown in Fig. 2. Generally, the products of the reaction of the carboxylic part of esters with $TiCl_4$ were qualitatively the same as those identified in the reaction of carboxylic acids with $TiCl_4$ (ref.[6]). Also, the proportions of the infrared band

FIG. 2

Infrared Absorption Spectra of $v(C=O)$ Region of Sec-butyl Dichloroacetate–$TiCl_4$ System in Benzene Solution

*1* Shortly after mixing the components; *2* after 20 hours. Absorption bands of $v(C=O)$ vibration: sec-butyl dichloroacetate (*cis, gauche* form) 1748, $1766 \, cm^{-1}$; $TiCl_4$. .ester $1670 \, cm^{-1}$; $CHCl_2COOTiCl_3$ 1590 sh, $1615 \, cm^{-1}$; $CHCl_2COOH.TiCl_4$ $1695 \, cm^{-1}$; $CHCl_2COOH$ (dimer, monomer) 1745, $1780 \, cm^{-1}$.
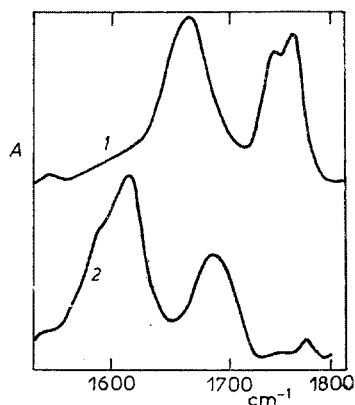
intensities of the carboxylate, the acid complex, and the free acid which depend on the strength of carboxylic acid[6] correspond in the acid − and ester − systems, except that the concentration of the free acid is lower in the latter systems.

According to the gas chromatographic analyses, the final alkylation products were mostly sec-butylbenzene with minor amounts of dialkylbenzenes. In the systems with tert-butyl esters the fast alkylation to di-tert-butylbenzenes was followed by a slower intermolecular alkyl shift reaction[7] giving the final ratio of tert-butyl-benzenes mono-/di-equal to 20. No alkyl isomerisations were observed.

The reported results gave us evidence of a different mechanism of alkylation from the mechanism proposed for esters of very strong acids[1,2] (Eq. (A)). Also, in the de-scribed case the formation of the complexes $TiCl_4$. ester causes further polarization of the ester bond O—R but at the same time it loosens considerably the Ti—Cl bonds in the complexed titanium tetrachloride, as it is demonstrated by the shift of $v(Ti—Cl)$ vibration by more than $70 \, cm^{-1}$ to a lower frequency. As a result of both effects, the formation of alkyl chloride (Eq. (B)) is preferred to the direct benzene alkylation (Eq. (C)).
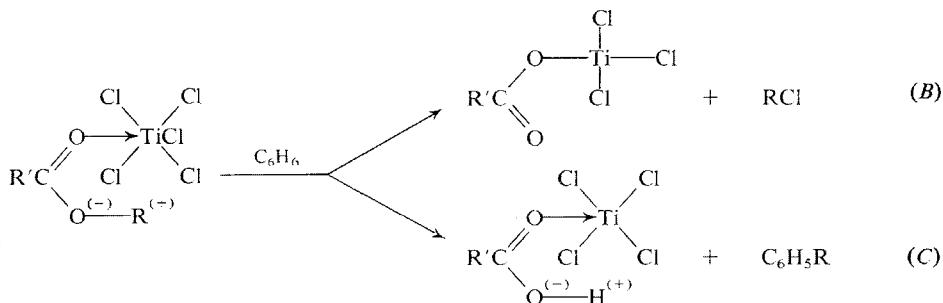
The time dependence of the ester, alkyl chloride, and alkylbenzenes concentrations, illustrated in Fig. 1, shows that the alkylation proceeds mainly due to the presence of alkyl chloride. The induction period and the shape of the decomposition curve of ester indicate the formation of an active catalyst in an autocatalytic reaction. Since the complexes $R'COOH.TiCl_4$ were found to be active catalysts for benzene alkylation with sec- and tert-butyl halides[7], we assume that the same complex (the formation of which in the systems with the esters was proved by IR spectra) catalyses the decomposition of the ester, too. Also, the disappearance of the induction period upon addition of carboxylic acid supports strongly this view. The decomposition of ester to alkyl chloride would then proceed through the formation of an inter-mediate oxonium salt formed by the action of strong complex acid on the ester[8], as shown in equation (D).

$$\text{[structure]} \longrightarrow \text{R}'\text{COOTiCl}_3 \;+\; \text{RCl} \;+\; \text{R}'\text{COOH} \qquad (D)$$
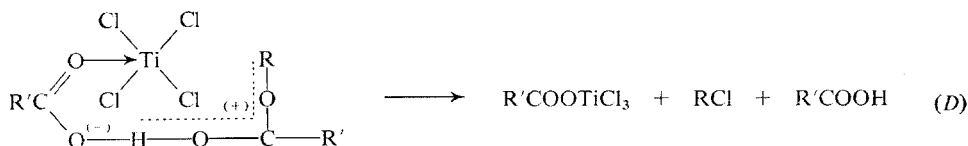
The interaction between carboxylic acids and $TiCl_4$ proceeds probably according to equation (E) and with increasing strength of the acids the first equilibrium is shifted to the left and the second to the right, thus giving a lower equilibrium concentration of the complex[6].

$$TiCl_4 \;+\; R'COOH \;\rightleftharpoons\; TiCl_4.R'COOH \;\rightleftharpoons\; R'COOTiCl_3 \;+\; HCl \qquad (E)$$

The catalytic amount of carboxylic acid could originate either in the reaction (C) or in the equilibrium (E). Also, the presence of proton containing impurities may initiate a series of decomposition reactions in which the carboxylic acid is evolved, though particulary no shortening of the induction period by water addition was observed.

It has been established[8] by the measurement of $H - D$ exchange rate with benzene that the acidity of $RCOOH.TiCl_4$ complexes increases in the order of the increasing strength of carboxylic acid from acetic to trifluoroacetic acid. In the same order the complexes catalyse the benzene alkylation with alkyl halides and isomerisation and intermolecular alkyl shift reactions[7]. The lower reactivity of sec-alkyl trifluoro-acetates in comparison with trichloroacetates (Table I) can be explained by a very low concentration of $CF_3COOH.TiCl_4$ complex in Eq. (E) (ref.[6]).

The comparison of $\Delta v(C{=}O)$ and the equilibrium constants K with the reactivity of the systems in Table I shows that the latter is not related to the strength of the electron–donor bond in the $TiCl_4 .$ ester complexes. The factors affecting the alkylation ability of the ester containing systems are in the order of importance: a) the ease of formation[9] and stability[10] of R^+ cations (tert-alkyl > sec-butyl > n-alkyl) b) the strength of the parent acid of the ester $(R'COOH, R'{-}CF_3 > CCl_3 > CF_2H > > CCl_2H > CH_2F > CH_2Cl > CH_3)$ c) the equilibrium concentration of the complex $R'COOH.TiCl_4$ $(R'{-}CCl_3 > CF_3)$ (ref.[6]).

Although, the alkylations with esters were described in several papers[1,2,11] the only mechanism so far suggested is expressed in Eq. (A). This mechanism supposes the dissociation of ester into acid anion and alkyl cation and describes very well the alkylations with esters of strong acids induced by SbF_5, BF_3 and $AlCl_3$. The action of $AlCl_3$ on carboxylic acid esters leads to formation of $(RCOO)_xAlCl_{3-x}$ and to considerable acetylation of aromatic hydrocarbons[12]. The present study of ester alkylations involving the two-step mechanism identified the intermediate alkyl chloride

as the true alkylation agent. This alkylation mechanism is limited to the less basic carboxylic acid esters with secondary and tertiary alkyls which are supposed to form alkyl chloride in the reaction with complex acid $TiCl_4 . RCOOH$ (Eq. (D)). The same complex acid is also very efficient catalyst for the subsequent alkylation of benzene with alkyl chlorides.

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