Kinetics and Mechanism of the Esterification of Carboxylic Acids Catalysed by Titanium Compounds

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INTRODUCTION

1.1 Metal-Catalysed Esterification

In liquid-phase esterifications, sulphuric acid has been the most widely accepted commercial catalyst, since, in most applications, it effects a greater rate of ester formation and larger percentage conversion of organic acid into ester than other well known esterification catalysts.

However, acid catalysis has certain disadvantages, as side reactions are a considerable problem. The presence of compounds produced by 'dehydration' with acid catalysts causes colour deterioration in the final product. The removal of these coloured compounds and of entrained acid is time-consuming and costly.

A catalyst which does not produce by-products is highly desirable. Various metallic compounds have been used for this purpose. Much of the available literature consists of patents and little is known about the mechanisms involved. The use of titanium compounds as esterification catalysts had been known for some time. They are of particular interest in the production of esters, which are used as plasticisers in the plastics industry. The presence of titanium compounds in the plasticiser does not affect adversely plastics such as polyvinyl chloride and therefore no consequential purification is necessary. Under most conditions, titanium compounds act as stabilisers, whereas the presence of strong mineral acid, arising from its use as an esterification catalyst, would have a harmful effect on polyvinyl chloride.

The effectiveness of titanium-containing esters, acylates and chelates as esterification catalysts is quite unexpected, as it is known that all these organotitanium compounds are hydrolysed by water, even at room temperature, at differing rates. The titanium alkoxides or titanic acid esters, which show great susceptibility to hydrolysis in the presence of water, are among the most effective organotitanium esterification catalysts. Thus the stability of the original organotitanium compound is not necessarily determinative of its catalytic activity. Armed with this knowledge a fundamental study of the kinetics and mechanism of esterification with titanium alkoxide catalysts was undertaken.
1.2 Alkaline and Acid-Catalysed Ester Hydrolysis and Acid-Catalysed Esterification.

(1.2.1) General

An alcohol and a carboxylic acid react together in the presence of a small amount of strong acid to form an ester.

\[ R^1CO_2H + R^2OH \xrightarrow{H^+} R^1CO_2R^2 + H_2O \] (1.1)

Since esterification is a reversible reaction, its mechanism has to be considered alongside that of the hydrolysis of esters. This topic has been much studied over the years by various workers. The earliest recorded study of the acid-catalysed reactions was the study of the reversible formation of ethyl acetate by Berthelot\(^2\). Warder\(^3\) (1881) studied the alkaline hydrolysis of ethyl acetate kinetically and observed second-order kinetics.

Polar effects of substituent groups were studied by Kindler\(^4\), who observed that electron-attracting groups accelerated the reaction, whilst electron-releasing groups retarded the alkaline hydrolysis of esters. Polar effects were found to be complicated by steric hindrance with the esters of aliphatic, arylaliphatic, and ortho-substituted benzoic acids. The above work has been fully summarised by Ingold\(^5\).

(1.2.2) Mechanism

The accepted classification of the possible mechanisms of carboxylic ester hydrolysis and formation is that of Ingold and Day\(^6\). They have based their mechanisms on the recognition of the following features:

(a) The type of attacking reagent: basic, neutral or acidic.
(b) Whether the reaction is unimolecular or bimolecular.
(c) Whether bond-fission occurs at the acyl—oxygen or the alkyl—oxygen bond.

The observed mechanisms are summarised in Table 1.1.
### TABLE 1.1

Known mechanisms of carboxylic ester hydrolysis and acid formation:

<table>
<thead>
<tr>
<th>Type of mechanism</th>
<th>Form Attacked</th>
<th>Reaction</th>
<th>Bond Fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>$R^1CO_2R^2$</td>
<td>Hydrolysis</td>
<td>$B_{AL1}$</td>
</tr>
<tr>
<td>Acidic</td>
<td>$R^1CO_2HR^{2+}$</td>
<td>Hydrolysis</td>
<td>$A_{AC1}$</td>
</tr>
<tr>
<td></td>
<td>or</td>
<td>Esterification</td>
<td>$A_{AC2}$</td>
</tr>
<tr>
<td></td>
<td>$R^1CO_2H^+$</td>
<td></td>
<td>$B_{AL}$ etc.</td>
</tr>
</tbody>
</table>

In the above notation B and A refer to basic and acidic reagents, the subscripts AC and AL refer to acyl—oxygen and alkyl—oxygen fissions respectively and the numerals indicate the molecularity of the mechanism.

Early mechanistic studies\(^5\) concentrated on differentiating between acyl—oxygen and alkyl—oxygen fission. The early workers hydrolysed esters which had a specific stereochemical configuration in R or had R as the neopentyl group, which if liberated would be rearranged. In each case R retained its identity suggesting acyl—oxygen fission occurred and not alkyl—oxygen fission. This evidence was extended by \(^{18}O\) isotope work introduced by Polanyi and Szabo\(^7\). The alkaline hydrolysis of n-pentyl acetate with water enriched in \(^{18}O\) as solvent was studied. They found no trace of \(^{18}O\) in the alcohol formed; therefore acyl—oxygen fission must have occurred.

\[
R^1CO^+_1 OR^2 + H^1_{18}OH \rightarrow R^1CO^+_{18}OH + R^2OH
\]  

(1.2)

The \(^{18}\)O isotope method has been used to study various ester hydrolyses and in each case acyl—oxygen fission has been found. The one exception was the alkaline hydrolysis of methyl 2,4,6-tri-t-butylbenzoate. The immense steric requirements of this substrate are not matched for any esters studied in the present work.
By far the most common mechanisms for simple alkyl esters with acidic or basic reagents are $\text{AAC}_2$ and $\text{BAC}_2$.

The $\text{BAC}_2$ mechanisms has been represented as a carbonyl addition reaction

$$\text{HO}^- + \frac{\text{C} - \text{OR}_2}{\text{R}_1} \xrightarrow{\text{slow}} \left[ \frac{\text{HO} - \text{C} - \text{OR}_2}{\text{R}_1} \right] \xrightarrow{\text{fast}} \frac{\text{HO} - \text{C} - \text{OR}_2}{\text{R}_1} \xrightarrow{\text{slow}} \text{HO}^- + \text{C} - \text{OR}_2 \quad (1.3)$$

or, as nucleophilic substitution at the carbonyl carbon

$$\text{HO}^- + \frac{\text{C} - \text{OR}_2}{\text{R}_1} \xrightarrow{\text{fast}} \left[ \frac{\text{HO} - \text{C} - \text{OR}_2}{\text{R}_1} \right] \xrightarrow{\text{slow}} \text{HO}^- + \text{C} - \text{OR}_2 \quad (1.4)$$

$$\text{R}_1\text{CO} - \text{CH} + \text{OR}_2 \xrightarrow{\text{fast}} \text{R}_1\text{CO} - \text{O}^- + \text{R}_2\text{CH} \quad (1.5)$$

The reaction goes completely to the right because of a fast, effectively irreversible proton transfer from the carboxylic acid formed, to a basic anion, to produce the carboxylate ion. The acidic reaction can be written

$$\text{H}_2\text{O} + \frac{\text{C} - \text{OH}_R}{\text{R}_1} \xrightarrow{\text{slow}} \left[ \frac{\text{H}_2\text{O} - \text{C} - \text{OH}_R}{\text{R}_1} \right] \xrightarrow{\text{fast}} \frac{\text{H}_2\text{O} - \text{C} - \text{OH}_R}{\text{R}_1} \xrightarrow{\text{slow}} \text{H}_2\text{O} + \text{C} + \text{RO} \quad (1.6)$$

The equilibrium position depends on the solvent composition.

The transition state for acyl—oxygen fission is formed more readily than the transition state for alkyl—oxygen fission because of the participation of the $\pi$ orbitals in the carbonyl group; although alkyl—oxygen fission occurs side by side, it is so much slower that it cannot be detected under most conditions.

A distinction between carbonyl addition and nucleophilic displacement mechanisms in acyl—oxygen fission cannot be made. The actual distribution of charge is likely to be in some way between the two extremes.

Bender has shown that addition complexes of carbonyl compounds exist with a lifetime long enough in comparison with a collision period, to be distinguised from an activated complex transition state. He hydrolysed
alkyl benzoates in aqueous dioxan or water enriched in $^{18}O$ and he compared the rates of exchange of oxygen between the medium and the ester (as determined in ester recovered after different amounts of partial hydrolysis) with the rate of hydrolysis. He found the rate of exchange to be from 10% to 40% (according to the ester and the medium) of the rate of hydrolysis. This shows that the intermediate complex lives long enough to survive the proton shift required to bring its two non-alkylated oxygen atoms into equivalence, so that either might split off to regenerate ester.

\[ \begin{align*}
18^0 \text{HO}^- + C\text{-OR}_2 \xrightarrow{k_1} & \quad 18^0 \text{HO}^- + C\text{-OR}_2 \\
R_1 & \quad R_1
\end{align*} \]

\[ \begin{align*}
18^0 \text{HO}^- + 18^0 \text{C}-\text{OR}_2 \xrightarrow{k_2} & \quad 18^0 \text{HO}^- + 18^0 \text{C}-\text{OR}_2 \\
R_1 & \quad R_1
\end{align*} \]

*Involves $^{18}$OH

\[ \begin{align*}
\text{HO}^- + C\text{-OR} \xrightarrow{k_3} & \quad \text{HO}^- + C\text{-OR} \\
R_1 & \quad R_1
\end{align*} \]

\[ \frac{k_{\text{exch}}}{k_{\text{hyd}}} = \frac{2 k_2}{k_3} \]

Similar results were found for the $A_{AC2}$ mechanism. The observed rate constant $k_{\text{obs}}$ for the above mechanism has been shown by Bender $^{10}$ to be a combination of the rate constants $k_1$, $k_2$ and $k_3$. Applying the steady-state treatment

\[ k_{\text{obs}} = \frac{k_1}{(k_2/k_3 + 1)} \]

As $k_2/k_3$ is always much smaller than unity, it can be assumed that partitioning of the intermediate complex between the processes corresponding to $k_2$ and $k_3$ has...
only a minor effect on the hydrolytic rate constant, $k_{obs}$, which will be approximately equal to the rate constant $k_1$ for the formation of the complex. The factors affecting the partitioning of the intermediate complex comprise the steric requirements of the groups, the polar character of $R$, and the basicity of the alkoxide anion $\text{II}$. The attacking nucleophile is considered by Bender $^{10}$ to approach the carbonyl group along a line approximately perpendicular to the plane of the group. The attained transition state would be established by the maximum possible overlap between the $\pi$ electron cloud of the carbonyl group and the relevant orbitals of the nucleophile.

The $\text{A}_{2}\text{C}_2$ mechanism can be represented as follows.

\[\begin{align*}
\text{R'}\text{OH}^{+} + \text{C}^-\text{OH} & \xrightarrow{k_1} \text{R}^{+} \text{OH} \quad \xrightarrow{k_2} \text{R}^{+} \text{OH}^{+} \\
\text{H}_2\text{O} + \text{C}^-\text{OR} & \xrightarrow{k_3} \text{H}_2\text{O}^- \text{C}^-\text{OR} \quad \xrightarrow{k_2} \text{HO}^- \text{C}^-\text{OH}^{+}
\end{align*}\]  

The evidence for placing the proton on the carbonyl oxygen is given by Aksnes and Prus $^{12}$ for acid catalysed ester hydrolysis and from studies of the state of carboxylic acids in solution in a concentrated sulphuric acid $^{13}$. Bender $^{10}$ applied the steady state treatment to this, giving the observed rate constant $k_{obs}$ in terms of the equilibrium constants $K_1$ and $K_2$ and the rate constants
\[ k_{\text{obs}} = k_1 \frac{k_1}{k_2} \left(1 + \frac{k_2}{k_3} \right) \]

Since \( k_2/k_3 \) is much smaller than unity and \( k_2 \) should be about unity, \( k \) is approximately equal to \( k_1 \).

1.3 The Polar and Steric Effects on Reactivity of Substituents in the Substrate

1.3.1 Polar Effects

A reaction centre may be affected in three ways. These are the direct field effect, the inductive effect and the mesomeric effect. Further time-variable effects may occur during the course of a reaction which reinforce the above effects, these are the inductomeric and electromeric effects. An alternative term often used for time-independent and time-dependent delocalisation effects collectively is resonance effect.

1.3.2 Direct Field Effect

The direct field effect, \( \phi \), can be described as the coulombic action on a reaction centre of a charged or dipolar substituent. The potential energy can be described by the expression

\[ \phi = \frac{m}{r^n} D \]

where

\( m \) = charge or dipole moment
\( r \) = separation distance
\( D \) = effective dielectric constant of the transmitting medium, i.e. molecular cavity and solvent.
\( n = 1 \) for unipolar substituents
\( n = 2 \) for dipolar substituents

An example of this is the effect of the \( \text{NMe}_3^+ \) substituent on a benzene ring.
(1.3.3) Inductive Effect

The inductive effect is the shift of electron density in a molecule due to successive polarisation of the bonds linking the substituent to the reaction centre. Both σ bonds and π bonds are capable of transmitting this effect through the corresponding σ-inductive and π-inductive effects. This effect can be shown by a halogen substituted benzene ring.

(1.3.4) Mesomeric Effect

The mesomeric effect is the displacement of electrons in a conjugated system due to the interaction of unshared p-electrons, or vacant p-orbitals, with the molecular orbital (i.e. π electron cloud) of the system. For example the nitro group in p-nitrobenzoic acid attracts electrons to itself in this manner as well as by the inductive effect. The ground state of this molecule is a resonance hybrid of the canonical structures shown below. The mechanism for the electron transfer can be represented as follows.

\[
\begin{align*}
\text{resonance hybrid} & \\
\text{Nitro group has an acid-strengthening effect on the carboxyl group.}
\end{align*}
\]
(1.3.5) The Relative Magnitude of Polar Effects

Substituents which are able to exert a polar influence by mesomerism are fairly well recognised. However the relative magnitude of the inductive and direct field effects of substituents has led to much disagreement. In an endeavour to clarify this, Roberts and Moreland\textsuperscript{14} carried out an important series of experiments. They studied the reactivities of a series of 4-substituted bicyclo-[2,2,2] octane-1-carboxylic acids

\[
\begin{array}{c}
\text{X} \\
\text{CO}_2\text{H}
\end{array}
\]

and their esters by measuring the acid dissociation constants in 50\% aqueous ethanol, rate coefficients for the reaction of the acids with diazodiphenylmethane, and rate coefficients for the alkaline hydrolysis of the ethyl esters. The system was chosen in an attempt to construct a model of the benzene system without the \(\pi\) electron system. The separation distance of the substituent and reaction centre are the same in each system.

Good linear free-energy relations were obtained, as found for the benzene system, and the substituent effects in the bicyclo-octane system were found to be very similar in magnitude to those found for the corresponding \textit{meta}-substituted benzene derivative. Roberts and Moreland therefore concluded that the \(\pi\) electron system in benzene does not play any significant role in the transmission of electrical effects from the \textit{meta}-position (excepting for mesomeric interactions). Further work\textsuperscript{15} on the bicyclo-octane system has supported Roberts and Moreland’s work.

(1.3.6) Steric Effects

Steric effects are due to the close approach of non-bonded atoms. The variation of potential energy as two non-bonded atoms approach each other is shown below;
Potential energy

Variation of energy of interaction of two non-bonded atoms with distance.

Dispersion forces\(^6\) cause attractions between non-bonded atoms; such attractions decrease with distance (i.e. \(\propto \frac{1}{r^6}\)). However, as the distance of separation becomes small an intense repulsion occurs, causing a sharp increase in energy. This energy, needed to compress the non-bonded atoms closely together, is called the non-bonded compression energy.

These non-bonded compressions are termed steric effects and may be sub-divided into kinetic and thermodynamic effects, depending on whether a rate of reaction or an equilibrium is affected. Those steric effects which are the direct result of non-bonded compressions are termed "primary steric effects". If the non-bonded compressions interfere with the transmission of polar effects in a molecule then the "secondary steric effect" is said to operate. For example, a bulky group substituted in a benzene ring will cause an adjacent nitro-group to be twisted out of the plane of the ring, thereby reducing the conjugation between the two. In this case the secondary steric effect has reduced the electron-withdrawing properties of the nitro-group. An actual example of this is the effect the two methyl groups in 2,6-dimethylnitrobenzene has on the nitro group.

The concept of steric hindrance has long been established. In the late 19th century, Meyer\(^7\) and his co-workers studied the esterification of substituted benzoic acids, and were unable to esterify 2,6-disubstituted benzoic acids,
regardless of the nature of the substituents. Enlarging on an earlier idea by Kehrmann\textsuperscript{18}, Meyer suggested that the approach of a reagent molecule could be hindered by the presence of bulky groups near the reaction centre. Rosanoff\textsuperscript{19} showed that equilibrium constants in esterification and hydrolysis for hindered and unhindered halogenated benzoic acids were comparable and that 2,6-disubstituted benzoic acids could be esterified at high temperatures. In fact, he was able to esterify 2,4,6-tribromo- and 2,4,6-trichloro-benzoic acid at 183°C.

The findings of Meyer were not developed further for 50 years, and during this time steric hindrance was thought of only in terms of the geometry of the initial states of reactants. Once the theory of organic reaction mechanisms had become established it became apparent that differences in non-bonded compressions between the transition state and the initial state must be considered. Usually in bimolecular processes, the transition state is more crowded than the initial state and therefore substituents which increase this crowding will cause steric retardation. The manner in which the primary steric effect influences a reaction may be judged from a consideration of Arrhenius parameters, or the related quantities of transition state theory\textsuperscript{20,21} (see Appendix).

A bulky substituent near the reaction centre may result in an increase in non-bonded compression energies as the transition state is formed. This will cause an increase in $\Delta H^\ddagger$. The substituent may also cause a reduction in the number of available energy levels of the transition state, relative to the initial state, and so lead to a reduction in $\Delta S^\ddagger$. Further, steric inhibition of solvation may occur, which will be more important in the more crowded transition state. This will increase $\Delta H^\ddagger$ by making the transition state less stable, relative to the initial state, and will increase $\Delta S^\ddagger$ by reducing the order of the transition state, relative to the initial state.

For reactions which proceed by a unimolecular mechanism, however, the transition state is less crowded than the initial state; in this case steric acceleration may be observed.
(1.4) Linear Free Energy Relationships

(1.4.1) General

In order to compare the rate constants and equilibrium constants for one set of reactions with those of another set for organic systems, empirical correlations have been much used. Correlation analysis takes the form of linear relationships involving logarithms of rate \(k\) or equilibrium \(K\) constants. These relationships are referred to as linear free-energy relationships; this term was first introduced by Hammett. An LFER can be defined as a linear relationship between the change in standard free energy involved in passing from an initial state to a final state \(\Delta G^0\) and the change in free energy involved in passing from an initial state to a transition state \(\Delta G^f\); that is

\[\Delta G^0 \propto \Delta G^f\] (1.10)

For equilibria, equation (1.11) applies

\[\log K = -\frac{\Delta G^0}{2.303RT}\] (1.11)

For chemical rate processes

\[\log k = \log \frac{RT}{N_A h} - \frac{\Delta G^f}{2.303RT}\] (1.12)

Where

- \(R\) = the gas constant.
- \(T\) = Kelvin scale temperature.
- \(N_A\) = Avogadro's constant.
- \(h\) = Planck's constant.

Correlation analysis in organic chemistry has been widely practiced since the early 1930s when Hammett at Columbia and Burkhardt at Manchester discovered linear relationships involving \(\log k\) and \(\log K\) for a number of systems. The Hammett equation was derived from this work. This treatment describes the influence of polar meta- or para-substitution on the side-chain reactions of benzene derivatives. However, this equation is unsatisfactory for ortho-substituted benzene derivatives and for substituted aliphatic systems where
steric factors play a part in the reaction. Here the Taft treatment has used correlation analysis to separate polar, steric, and resonance effects. The two treatments of data have led to an increased understanding of the effect of molecular structure on chemical reactivity.

(1.4.2) The Hammett Equation

The Hammett equation takes the form

$$\log k = \log k^0 + \rho \sigma$$

or

$$\log K = \log K^0 + \rho \sigma$$

where $k$ or $K$ is the rate or equilibrium constant respectively for a side-chain reaction of a meta- or para-substituted benzene derivative. The symbol $k^0$ or $K^0$ denotes the statistical quantity approximating to $k$ or $K$ for the unsubstituted compound. The substituted constant $\sigma$ measures the polar effect (relative to hydrogen) of the substituent (in a given position, meta or para) and is in principle independent of the nature of the reaction. The reaction constant $\rho$, depends on the nature of the reaction (including conditions such as solvent and temperature) and measures the susceptibility of the reaction to polar effects.

Hammett chose the ionisation of benzoic acids in water at 25°C as a standard process for which $\rho$ is defined as 1.000. The value of $\sigma$ for a given substituent is $\log \frac{K_a}{K_a^0}$ where $K_a$ is the ionisation constant of the substituted benzoic acid and $K_a^0$ is that of benzoic acid itself. In order to make a Hammett plot, several meta- or para-substituted compounds, of known $\sigma$, belonging to the same system must be employed. The logarithms of rate or equilibrium data are plotted against $\sigma$, the slope of the best straight line gives $\rho$, and the intercept gives $\log k^0$ or $\log K^0$.

The Hammett treatment does not give good results for all the systems studied. Jaffe showed the Hammett treatment gave satisfactory results in about 70 per cent of the 400 systems he considered. This study was on the basis of a statistical treatment. Marked deviations from the Hammett equation often occur with para-substituents of considerable positive or negative resonance effect. This can be explained by cross-conjugation involving...
The free base is stabilised by delocalisation of electrons involving the canonical structure (I) Figure I.

It is now necessary to assign special substituent constants, $\sigma^+$ for $-M$ or $-E$ and $\sigma^-$ for $+M$ or $+E$. $\sigma$ values for the above systems may also vary for meta-substitution by the relay effect and special values for $\sigma^+_m$ and $\sigma^-_m$ are determined.

The contribution of the resonance effect of a substituent relative to its inductive effect varies as the electron-demanding quality of the reaction centre is varied. There have been several modifications of the Hammett equation to allow for this. Yukawa and Tsumo proposed a method for dealing with substituents with large $+E$ and $+M$ effects in their influence on reactions which are more electron-demanding than the ionisation of benzoic acid. They modified the Hammett equation as follows.

$$\log k = \log k^0 + \rho \left[ \sigma + r (\sigma^+ - \sigma^-) \right]$$

or

$$\log K = \log K^0 + \rho \left[ \sigma + r (\sigma^- - \sigma^+) \right]$$

Here $r$ is a constant giving the contribution of the enhanced resonance effect for the substituent. This equation has been applied to numerous reactions and has often been more successful than the Hammett equation. The corresponding equation with $\sigma^-$ constants to deal with the influence of $-M$ and $-E$ substituents on reactions which are less electron-demanding than the
The ionisation of benzoic acid was formulated by Yoshioka, Hamamoto and Kubota.

\[ \log k = \log k^0 + \rho \left[ \sigma + \frac{x}{r} (\sigma^- - \sigma^+) \right] \]

or

\[ \log K = \log K^0 + \rho \left[ \sigma + \frac{x}{r} (\sigma^- - \sigma^+) \right] \] (1.15)

The applications of this have not been so well explored, but it has been applied to various processes.

Van Bekkum, Verkade and Wepster strongly criticised the duality of sigma constants as an artificial device to describe cross conjugation. They proposed the use of \( \sigma^N \) for each substituent, which they selected as a 'normal' value. These were calculated from the individual \( \sigma \) values for a substituent in about eighty reaction series. The assumption was made that \( +M \) and \( +E \) reaction centres gave normal sigma values for \( +M \) and \( +E \) substituents and \( -M \) and \( -E \) reaction centres gave normal sigma values for \( -M \) and \( -E \) substituents, a small spread of calculated \( \sigma^N \) values being averaged for each substituent. This work was important but it tends toward the situation in which the 'substituent constant' becomes reaction dependent and correlation analysis is devalued.

Large deviations from the Hammett equation and its refined forms can be observed when complex reaction mechanisms occur. This may happen if the observed rate constant is effectively an overall rate constant arising from two or more competing mechanisms or is really a complex function of rate constants for a series of reaction steps.

\( \Delta(1.14-3) \) The Taft Treatment

The failure of the Hammett equation for aliphatic and ortho-substituted aromatic systems is attributed to steric effects occurring as well as polar effects. Kindler and later Ingold suggested methods of separation for steric and polar effects. Following Ingold, Taft devised a procedure for separating polar, steric, and resonance effects based on an analysis of the rate coefficients of basic and acidic hydrolysis of esters, thus enabling correlation analysis to be applied to these systems.
Taft suggested the following equation for evaluating the polar effect of a substituent $R'$ in the ester $R'CO_2R^2$

$$
\sigma^* = \left[ \log \left( \frac{k}{k^0} \right)_B - \log \left( \frac{k}{k^0} \right)_A \right] / 2.48
$$

(1.16)

$\sigma^*$ is a polar substituent constant for $R$. The rate constant $k$ refers to reactions of $R'CO_2R^2$ and $k^0$ to those of $MeCO_2R^2$ as standard. $B$ and $A$ refer to basic and acidic hydrolysis carried out with the same $R^2$, solvent and temperature. The factor 2.48 puts the $\sigma^*$ value on about the same scale as Hammett's $\sigma$. The equation may also be applied to ortho-substituted benzoic esters with the ortho-methyl ester as standard. $\log \left( \frac{k}{k^0} \right)_B$ measures the sum of the polar, steric, and resonance effects of $R'$. The difference between these two terms gives the polar effect of $R'$.

The steric substituent constant $E_s$ can be defined as

$$
E_s = \log \left( \frac{k}{k^0} \right)_A
$$

(1.17)

In conjugated systems $E_s$ contains a resonance contribution. $E_s$ is a measure of the combined potential energy and kinetic energy effects. When the initial state with $sp^2$ hybridisation at the carboxy-carbon is converted into the transition state with near $sp^3$ hybridisation, there is (i) an increase in repulsions between non-bonded atoms (a potential energy effect), (ii) an increase in mutual interference of groups or atoms with each other's motions (a kinetic energy effect). Both of these contribute to the free energy of activation.

Taft's treatment is based on the following assumptions

(1) The relative free energy of activation $\Delta \Delta G^+_t$ may be treated as the sum of independent contributions from polar, steric, and resonance effects.

(2) In the corresponding acidic and basic reactions, the steric and resonance effects are the same. The transition states for the acidic and alkaline reactions differ only by two protons.
The difference in the steric interactions of the substituent $R_1$ in the corresponding transition states for the acidic and alkaline reactions should be essentially constant because of the small size of the proton.

(3) The polar effects of substituents are markedly greater in the alkaline than in the acidic reaction. This can be inferred from the $\rho$ values obtained from the Hammett treatment of reactions involving meta- or para-substituted benzoates. For alkaline hydrolysis $\rho$ values are commonly in the range +2.2 to +2.8 and for acidic hydrolysis in the range 0 ± 0.5.

Values of $\sigma^*$ are positive for electron-withdrawing substituents and negative for electron-releasing substituents. The effect of branching at the $\alpha$-carbon atom of alkyl groups leads to a negative value of $\sigma^*$ depending on the supposed electron-releasing effect of the group. Branching at the $\beta$ carbon atom or at carbon atoms further along the carbon chain has a relatively small effect on the $\sigma^*$ value.

Taft found that the rate or equilibrium constants for a wide variety of reactions conformed to equations (1.18).

$$\log \left( \frac{k}{k_0} \right) = \rho^* \sigma^*$$

or $$\log \left( \frac{K}{K_0} \right) = \rho^* \sigma^*$$

(1.18)

Here $\rho^*$ is the reaction constant analogous to the Hammett $\rho$ constant. Some reactions of ortho-substituted aromatic systems also obey these equations.

Conformity to these equations implies that all effects other than polar remain near constant throughout each reaction series. Steric effects of substituents are either completely absent or approximately the same as the
steric effect of a methyl group (the standard) within the range considered.

The equation

$$\log \left( \frac{k}{k_0} \right) = \rho^* \sigma^* + \delta E_s$$

or

$$\log \left( \frac{k}{k_0} \right) = \rho^* \sigma^* + \delta E_s$$  \hspace{1cm} (1.19)

is the most general equation because both polar and steric effects are considered. This equation was devised by Pavelich and Taft\textsuperscript{27}, and has found applications in several reactions.

1.5 Some Chemistry of Organotitanium Compounds

(1.5.1) The Molecularity of Titanium Alkoxides

Probably the most important structural feature of the titanium alkoxides is that they are usually polymers, although monomeric species are known, especially in very dilute solution. Solid titanium tetraethoxide is a tetramer, each Ti atom attains octahedral co-ordination. In benzene primary titanium alkoxides are dimeric or trimeric\textsuperscript{28}, but secondary and tertiary alkoxides are monomeric. A glance at a table of physical properties will show that in a series of isomeric titanium alkoxides there is a gradual reduction in the boiling-points with increasing branching of the carbon chain. This is probably because the continuous-chain titanates tend to form intermolecular co-ordinate linkages between the oxygen atoms of the alkoxy groups and the titanium atoms\textsuperscript{29}. This is supported by ebullioscopic determinations of the molecular weights\textsuperscript{30-34}, and by cryoscopic methods\textsuperscript{30,35}, which showed that whereas titanium-n-alkoxides are trimeric and dimeric in benzene, tertiary titanium alkoxides are monomeric in the same solvent. Wardlaw\textsuperscript{34} and his co-workers concluded that the degree of intermolecular co-ordination is almost independent of chain length.

From his work, Bradley\textsuperscript{29} concluded that the degree of association is the lowest possible to enable all the titanium atoms to have their maximum co-ordination number. This agrees with the work of Caughlan\textsuperscript{35} and his
colleagues who suggested a structure based on hexa-co-ordinated titanium for titanium tetraethoxide, which they also found to be trimeric. Earlier Bradley and Wardlaw\(^{34}\) had shown that normal titanium alkoxides are monomeric in the vapour state, and that in a series of such alkoxides the entropy of vaporisation increases with chain length. They concluded that this is probably due to the degree of 'molecular entanglement'.

Nesmeyanov, Nogina, and Dubovitskii\(^{36}\) found a variation of the molecular weight with time in benzene solution of ethoxides, butoxides and hexoxides, and that the degree of association decreases, so that after several hours the substances behave as monomers.

(1.5.2) Hydrolysis of Titanium Alkoxides

Titanium alkoxides are exceedingly readily hydrolysed even by traces of water; such reactions give polymeric species with $-\text{OH}$- or $-\text{O}$- bridges.

This probably occurs as follows.

\[
\begin{align*}
\text{Ti(OR)}_4 + \text{H}_2\text{O} & \rightarrow \text{Ti(OR)}_3 + \text{ROH} + \text{H} \rightarrow \text{TiOH(OR)}_3 + \text{ROH} \\
2(\text{RO})_3 \text{TiOH} & \rightarrow (\text{RO})_3 \text{Ti} - \text{O} - (\text{OR})_3 + \text{H}_2\text{O}
\end{align*}
\]

Complete hydrolysis to hydrated titanium dioxide is effected only with great difficulty.

Bistean and Comory\(^{37}\) found that resistance to hydrolysis increased greatly with increasing chain-length. Winter\(^{38}\) also showed that in a series of isomeric titanium alkoxides the tertiary alkoxide is hydrolysed more readily than the secondary, and the secondary more readily than the primary. The rate of hydrolysis of titanium tetra-n-butoxide increased with increase of temperature\(^{39}\). Moreover, the higher the water/titanium ratio the more rapid the rate of hydrolysis.
The hydroxyester formed in equation (1.20) is not isolable, as it reacts immediately with a further molecule of hydroxyester to give the condensed ester in equation (1.21). Boyd and Winter showed that the ratio of water to titanium compound affected not only the rate of hydrolysis of titanium butoxide and ethoxide, but also the degree of hydrolysis. As long as the ratio of water to alkoxide does not exceed unity the product apparently consists of a linear polymer, the reaction proceeding according to the equation (1.22).

\[ n \text{Ti} (\text{OR})_4 + (n - 1) \text{H}_2\text{O} \rightarrow (\text{RO})_2(n + 1) \text{Ti}_n \text{O}_n - 1 + 2(n - 1) \text{ROH} \]  

(1.22)

At higher water concentrations cross-linked polymers are obtained. Boyd, Gaze and Wardlaw found that hydrolysis with aqueous alcohols in boiling titanium alkoxide solutions in the same alcohols, gave polymers of a low degree of polymerisation and concluded that this was due to solvation, and that the results were consistent with a co-ordination value of six for titanium. However, other evidence concerning the products of hydrolysis offered by different authors is conflicting.

(1.5.3) The Reaction of Titanium Alkoxides with Carboxylic Acids

Titanium alkoxides react with carboxylic acids to form mono- and di-acylates, but so far simple tri-acylates or tetra-acylates have not been prepared in this manner. The reaction of one or two molecules of carboxylic acid proceeds readily, by a mechanism which is probably similar to that of hydrolysis of titanium alkoxides. However, further reaction is difficult and condensation takes place, with the formation of polytitanyl acylates. Even mono- and di-acylates are not stable, but decompose slowly at room temperature, and more rapidly on being warmed to give condensed esters or polyalkoxytitanyl acylates, together with organic esters.

Pande and Mehrotra found that on treating titanium alkoxides with two moles of a fatty acid, a rapid reaction occurred with two moles of alcohol being expelled. The product obtained corresponded in analysis to a titanium dialkoxy diacylate. When titanium dibutoxy dipalmitate was further treated with palmitic acid in a molar ratio of 1:1, 0.8 moles of butan-1-ol were distilled out. The
resulting products were treated with dry acetone. The insoluble titanium soap so obtained, corresponded on analysis, to a mixture of

$$\text{TiO(O}_2\text{CR}_2^2\text{)}_2 \quad \text{and} \quad 0\left[\text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_2\right]_2$$

in the molar ratio of 8:1. The acetone-soluble portion was found to be a mixture of fatty acid and its ester

$$\text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_3 + 0\text{R}_1\text{OH} \quad (1.23)$$

$$\text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_3 \rightarrow \text{TiO(O}_2\text{CR}_2^2\text{)}_2 + \text{R}_2^2\text{CO}_2\text{R}_1$$ \quad (1.24)

$$\text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_3 + \text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_2 \rightarrow 0\left[\text{Ti(OR)}_1\left(\text{O}_2\text{CR}_2^2\right)_2\right]_2 + \text{R}_2^2\text{CO}_2\text{R}_1 \quad (1.25)$$

The decomposition in (1.24) appeared to be much faster (about eight times) than that in (1.25) and hence, the final products are formed in a molar ratio of 8:1. Further, titanium isopropoxide was treated with an excess of each of several lower carboxylic acids. The organic esters formed in these reactions were removed by distillation under reduced pressure. The end product from acetic acid was found to be an equimolar mixture of TiO(O_2CCH_3)_2 and 0[Ti(O_2CCH_3)_3]_2, while with propionic acid a mixture of TiO(O_2CC_2H_5)_2 and 0[Ti(O_2CC_2H_5)_3]_2 in the molar ratio of 4:1 was obtained. The above observations indicate that the reaction (1.24) becomes more dominant as the length of the carbon chain of the carboxylic acid increases.

In an attempt to produce tri-acylates and tetra-acylates, Pande and Mehrotra treated one mole of titanium alkoxide with between four and five moles of carboxylic acid in benzene, the alcohol produced being continuously removed azeotropically. Approximately three moles of alcohol only could be distilled out per mole of alkoxide. The difficult removal of the fourth alkoxy group was explained on the basis of steric hindrance exhibited by the presumed oxygen bridge structures. The associated nature of monoalkoxytri-soaps of titanium may involve the following type of donor bondings.
The titanium atoms in this molecule are so sterically crowded that the co-ordination of another carboxylic acid molecule under ordinary conditions becomes impossible and no further replacement can be achieved.

1.6 Catalysis by Metal Complex ions

(1.6.1) General

Metal ions can produce powerful accelerations of reactions in homogeneous solution. Catalysis occurs because the metal ion has the ability to co-ordinate with the substrate and thereby stabilise the relevant transition state. However, the mode of action of metal ions in the stabilisation of transition states is varied. In some reactions, the metal ion acts as a "superacid" catalyst; that is, it serves as a proton of magnified charge. In other reactions, the metal ion serves as a carrier of electrons, and in some reactions the metal ion forms a metal-carbon bond and participates directly in the co-valent bond changes. In many instances, the metal ion acts as a template on which reactants can bind and react. Metal ions may have in general, square-planar, tetrahedral, or octahedral co-ordination. These complexes may be of the low- or high-spin variety.

The hydrolysis of many esters is subject to catalysis by metal ions. Structurally these esters have one common feature: they contain a secondary functional group that can serve as a ligand for the metal ion. An example of such a reaction is the hydrolysis of α-amino esters catalysed by Cu\(^{2+}\) ions which can take place in two ways, in which the metal ion complexes with the carbonyl oxygen atom (1.25), or alternatively the alkoxy oxygen atom (1.27) of the ester:
An alternative explanation can also account for the metal-ion catalysis. Since cupric ion complexes hydroxide ion around neutrality\textsuperscript{46,47}, the catalysis can consist of a template-like reaction in which the cupric ion binds both the substrate and hydroxide ion, leading to an intracomplex reaction of hydroxide ion with the ester.

(1.6.2) Metal-catalysed esterification

The literature available for the metal-ion catalysis of esterification is mainly concerned with the reactions of dicarboxylic acids with monohydric alcohols, or of monocarboxylic acids with 1,2 diols as these are the sources of the most important industrially used esters. It has been postulated for esterification of glycols with aromatic carboxylic acids that the metal oxides, acetates, oxalates or benzoates are transformed under esterification conditions by an
equilibrium reaction with the aromatic carboxylic acid or glycol into a complex, presumably that of the metal compound with the acid, or more likely a complex of the acid with the metal glycolate, for example

\[
(RCOO)_x M \left[ O(\text{CH}_2)_n \text{OH} \right]_y
\]

This complex reacts in the rate-determining step with another glycol molecule to form the corresponding ester with regeneration of the catalyst\(^4\). In none of the catalysed reactions, has an induction period been observed; this indicates that the formation of the intermediate complex is rapid and takes place at the very beginning of the esterification. The rate enhancement of esterification of benzoic acid with ethylene glycol has been observed with di-n-butyltin oxide\(^49\) and titanium tetraalkoxides\(^50\) which are known to react with ethylene glycol to form the corresponding glycol oxides of complex structure. Tetra-n-butylin, which does not act as a catalyst in this case, does not react with ethylene glycol even at elevated temperatures, to give a glycolate of tetravalent tin.

The complex should not be too stable. Metal ions such as Sb\(^{3+}\), although resistant to poisoning by carboxylic derivatives\(^51\), also show low activity in the esterification of benzoic acid carried out in a great excess of a 1,2 diol. The kinetics of reactions involving 1,2 diol, carboxylic acid, and various compounds of Group II - V, VII and VIII metals have been found to be of half-order both in the monocarboxylic acid and in metal compound\(^48\). The uncatalysed reaction was first-order in the acid and zeroth-order in diol with a large excess of diol.

Studies of reactions between ortho-, meta- and para-substituted benzoic acids and ethylene glycol using lead II oxide, which exhibits a lower catalytic activity than titanium IV and tin II compounds at 197°C, revealed pseudo-half-order kinetics in all cases\(^52\).

\[
k_0 = 2 \left( [A]_0^{1/2} - [A]^{1/2}/t \right) (1.28)
\]
\[ k_0 = \text{pseudo-half-order constant} \]
\[ A = \text{an ortho-, meta- or para- substituted benzoic acid} \]
\[ \circ \text{ signifies initial concentration.} \]

The nucleophilic character of the esterification was shown by electron-attracting substituents accelerating and electron-donating substituents retarding both the uncatalysed and metal ion-catalysed esterification of meta- and para-substituted benzoic acids. Both esterifications are therefore facilitated by low electron density at the reaction site. The observed reaction rates indicated the following order of reactivity.

\[ p \text{ NO}_2 > m - \text{NO}_2 > m - \text{CF}_3 > p \text{Cl} \approx p - \text{Br} > H > m - \text{CH}_3 \]

\[ p \text{ CH}_3 >> p \text{OCH}_3 \]

The plot of logarithms of pseudo-half-order rate constants, \( k_0 \), for the \( \text{Pb}^{2+} \) catalysed esterification of meta- and para-substituted benzoic acids against Hammett \( \sigma \) constants gave an excellent linear dependence (\( r = 0.9958 \)) with the exception of \( p \)-methoxybenzoic acid. The reaction constant \( \rho \) was 0.44 ± 0.02.

The plot of logarithms of rate constants for the uncatalysed esterification of meta- and para-substituted benzoic acids against \( \sigma \) gave a satisfactory linear dependence (\( r = 0.9876 \)), again with the exception of \( p \)-methoxybenzoic acid; in this case the reaction constant \( \rho \) had a value of 0.46 ± 0.03.

In the preparation of dialkyl phthalates from phthalic anhydride, titanium alkoxides are not very good esterification catalysts at 150°C, (see fig. 1.1), but at 200°C they become quite effective (see fig. 1.2). Even at 200°C the reactions are not quite as rapid as with sulphuric acid but the colour of the esters produced is much better. The colour of the product after 99.5% conversion is the same as that after 93% conversion, although the reaction time is twice as long. Very high conversions are achieved by using titanium alkoxides. The conversion into monoester is very fast, and is complete by the time the phthalic anhydride has dissolved and the temperature has reached 200°C. The formation of
diester is much slower. When the rate is measured in terms of conversion of the half-ester, the reaction is found to be first-order with respect to monoester up to at least 90% conversion at 200°C (see fig. 1.3).

1.7 The Scope and Plan of the Present Work

The initial system chosen for study was titanium tetra-n-butoxide, acetic acid and butan-1-ol. Titanium tetra-n-butoxide was selected as the catalyst as it is the first relatively stable member of the titanium alkoxide homologous series and it is also commercially available. Acetic acid was selected as the acid because of its suitable physical properties and also many data on kinetics and mechanism of esterification are available for this acid. Butan-1-ol was selected as the alcohol in order to keep the system as simple as possible for a kinetic and mechanistic study.

The complex nature of the kinetics obtained from the above system due to the instability of titanium tetra-n-butoxide to water which is generated during esterification, brought about a search for a more stable catalyst.

Titanium alkoxides which have chelating ligands present are known to be more stable to hydrolysis than simple alkoxides. Titanium bis-(triethanolamine) diisopropoxide (TiTE), which is available commercially, was found to give a simpler kinetic picture. Because of this a detailed study of this as a catalyst in the reactions of acetic acid and butan-1-ol was undertaken. Finally a brief study of some other titanium alkoxide catalysts was made.

In this thesis the TiTE catalyst system will be discussed initially, then the titanium tetra-n-butoxide catalyst system and finally some other titanium alkoxide catalysts will be briefly considered.
Fig. (1.1) Nonyl phthalate preparation: Various catalysts at 150°C compared with titanium tetra-n-butoxide at 200°C.

1. Titanium tetramethoxide.
2. Titanium tetraisopropoxide.
3. Toluene-p-sulphonic acid.
4. Sulphuric acid. (1 - 4 at 150°C)
5. Titanium tetra-n-butoxide at 200°C.

All at 1.0 molar % concentration based on phthalic anhydride.
Fig. (1.2) Nonyl phthalate preparation: various catalysts at 200°C.

1. Titanium tetramethoxide.
2. Titanium triethanolamine.
3. Titanium tetra-n-butoxide.
4. Toluene-p-sulphonic acid.
5. Sulphuric acid.

All at 1.0 molar%
Fig. (1.3) Nonyl phthalate preparation at 200°C: results with two catalysts plotted as for a first-order reaction.

Sulphuric acid. ○
Titanium tetra-n-butoxide. ●

\[ C_0 = \text{initial concentration of half-ester.} \]

\[ C_t = \text{concentration of half-ester after t minutes.} \]
EXPERIMENTAL

2.1 Preparation and Purification of Materials

(2.1.1) Substituted Benzoic Acids

The benzoic acids used in this investigation were those prepared or purified by previous workers. These acids were used without further purification. The origins of these acids and their purities are listed in Table (2.1). The methyl ester of each acid was assayed by g.l.c., and was prepared by adding an ethereal solution of diazomethane to an ethereal solution of the acid. Further, the equivalent weight of each acid was determined by titration. It was always found to be within 1 per cent of the calculated value.

(2.1.2) Substituted Acetic Acids

These were prepared or purified by previous workers and were analysed by the methods used for the substituted benzoic acids in (1). The origins and purities of these acids are listed in Table (2.2).

(2.1.3) Titanium Alkoxides

The six titanium compounds used as catalysts were supplied by Titanium Intermediates Limited. The purity of each sample was checked by the colorimetric analysis technique of Weller54 (page 43). The results are given in Table (2.3). All six titanium compounds were stored under nitrogen in a 'dry-box', because they are all to some extent hydrolysed in moist air.

(i) Titanium Tetramethoxide

This was supplied as a white solid damped by a small quantity of methanol and propan-1-ol.

(ii) Titanium Tetraethoxide

This was supplied as a pure liquid.

(iii) Titanium Isopropoxide

This was supplied as a colourless liquid containing free propan-2-ol.

(iv) Titanium Tetra-n-butoxide, Bis(triethanolamine) Titanium Di-isopropoxide (TiTE) and Di-isopropoxytitanium Bis (acetylacetonate) (Ti Acac)
These compounds as supplied contained free alcohol to facilitate handling, because all three are highly viscous in their pure form. They are all fairly stable in moist air. For each material, free alcohol was removed under reduced pressure until only sufficient alcohol remained to enable the material to be handled easily. Titanium tetra-n-butoxide is a yellow liquid and was supplied containing 20 per cent free butan-1-ol. TiTE is also a yellow liquid and was supplied containing 20 per cent of propan-2-ol. Ti AcaO is a red liquid and was supplied containing 25 per cent of propan-2-ol.

In Table (2.3) values exceeding 100 per cent for the titanium analysis are due to the presence of other titanium species in the material. The nature of these species is not fully understood but it is likely they contain \(-\text{Ti-O-Ti-}\) linkages.

(2.1.4) Butan-1-ol

Smith's method was used to dry butan-1-ol. Sodium (12 g) was dissolved in butan-1-ol (1.61). When the evolution of hydrogen ceased, dibutyl phthalate (54 cm.\(^3\)) was added and the mixture was heated under reflux for 2 hours. Fractional distillation gave butan-1-ol of b.p. 117.4-117.9° (lit. 117.7°). The water content of each batch of solvent was determined, before use, by titration with Karl Fischer reagent; water content was always less than 0.01 per cent v/v. Because of its hygroscopic nature butan-1-ol was stored under nitrogen in a 'dry-box'.

(2.1.5) Potassium Acetate

This was commercially available and had m.p. of 299°C (lit. 300-301°C).

(2.1.6) Potassium Trifluoroacetate

A solution of potassium trifluoroacetate (0.25M) in butan-1-ol (100 cm.\(^3\)) was prepared. Pure trifluoroacetic acid (2.86 cm.\(^3\)) was pipetted into butan-1-ol (50 cm.\(^3\)), potassium (0.975 g.) was dissolved in butan-1-ol (50 cm.\(^3\)) and the two solutions were mixed carefully to produce potassium trifluoroacetate. The solution was shown to be neutral by use of a pH meter.
(2.1.7) Triethanolamine

This was commercially available and had m.p. 19-20°C (lit. 21.2°C).

(2.1.8) Potassium Methoxide

This was prepared for use as a titrant by dissolving the required amounts of potassium hydroxide pellets in 'A.R.' puriss methanol.

**TABLE (2.1)**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
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<td>Benzoic</td>
<td>99.5</td>
<td>122</td>
<td>122-123</td>
<td>D</td>
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<tr>
<td>p- Chlorobenzoic</td>
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<td>243</td>
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<td>178</td>
<td>181-182</td>
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<td>241-243</td>
<td>242.4</td>
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<tr>
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<td>179-181</td>
<td>182</td>
<td>E</td>
</tr>
<tr>
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<td>155-156</td>
<td>155-158</td>
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<tr>
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<td>110-112</td>
<td>111.3</td>
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<td>146-148</td>
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<tr>
<td>p- Chlorobenzoic</td>
<td>99.5</td>
<td>143</td>
<td>142</td>
<td>A</td>
</tr>
</tbody>
</table>

A - Dr. A. Buckley
B - Mr. R. Wilkinson
C - Dr. J. H. P. Utley
D - Dr. M. H. Aslam
E - Commercially available.
### TABLE (2.2)

**Purities of the Substituted Acetic Acids**

<table>
<thead>
<tr>
<th>Acid</th>
<th>G.L. C. (methyl ester) percentage purity</th>
<th>M.p. or B.p. °C</th>
<th>M.P.or E.p. (Lit.) °C</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>98.9</td>
<td>117 (b.p.)</td>
<td>116-118 (b.p.)</td>
<td>B</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>99.1</td>
<td>63</td>
<td>61-62</td>
<td>A</td>
</tr>
<tr>
<td>3-Chloropropionic</td>
<td>99.5</td>
<td>40</td>
<td>38-41</td>
<td>A</td>
</tr>
<tr>
<td>2,2-Dimethylpropionic</td>
<td>99.92</td>
<td>32-34</td>
<td>33-35</td>
<td>A</td>
</tr>
<tr>
<td>2-Methylpropionic</td>
<td>99.3</td>
<td>151-153</td>
<td>153-154</td>
<td>A</td>
</tr>
<tr>
<td>Phenoxyacetic</td>
<td>99.7</td>
<td>98</td>
<td>98-100</td>
<td>B</td>
</tr>
<tr>
<td>Phenylacetic</td>
<td>99.2</td>
<td>76-77</td>
<td>770-785</td>
<td>B</td>
</tr>
<tr>
<td>2-Phenylpropionic</td>
<td>98.8</td>
<td>265 (b.p.)</td>
<td>260-262</td>
<td>B</td>
</tr>
<tr>
<td>Propionic</td>
<td>98.5</td>
<td>142 (b.p.)</td>
<td>141 (b.p.)</td>
<td>A</td>
</tr>
</tbody>
</table>

A - Mr. R. Wilkinson  
B - Mr. R. A. Kidd

### TABLE (2.3)

**Purities of the Titanium Alkoxides**

<table>
<thead>
<tr>
<th>Percentage Purity (based on monomer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(OCH₃)₄</td>
</tr>
<tr>
<td>Ti(OC₂H₅)₄</td>
</tr>
<tr>
<td>Ti(O Pr)₄</td>
</tr>
<tr>
<td>Ti(O Bu)₄</td>
</tr>
<tr>
<td>TiTE</td>
</tr>
<tr>
<td>Ti Acac</td>
</tr>
</tbody>
</table>
(2.2) The Study of the Kinetics of Esterification

(2.2.1) pH Measurements

The decrease in acidity with time during the course of an esterification was followed by automatic titration with a Radiometer 26 pH meter. The electrodes used were an Auchtermuchty 4.80 glass electrode and a calomel electrode containing a saturated solution of potassium chloride in methanol. The pH meter was standardised by using buffer solutions of pH 5.00 ± 0.1 and pH 9.00 ± 0.1 which were supplied by B.D.H. Chemicals Ltd. The titrant used was potassium methoxide (0.05M). It was necessary to use an organic base to avoid precipitation of hydrated titanium oxide during titration. Preliminary experiments showed that this would produce erroneous results due to the glass-electrode surface becoming coated. Potassium methoxide was employed as opposed to sodium methoxide as the titrant because the presence of sodium ions causes the glass electrode to cease to function as an indicator electrode.

In certain cases, Harlow has shown that potassium ions at the glass electrode surface can produce ill-defined titration curves due to a decrease of the voltage change at the end-point. The curves of pH versus volume of titrant for varying concentrations of acetic acid and titanium alkoxide in butan-1-ol were studied in order to observe the effect of titanium alkoxide concentration. In no case was the effect mentioned by Harlow observed. However, the effect of increasing the titanium alkoxide concentration was to flatten the pH curves, see the example in Fig. (2.1) giving a less well defined end-point. The addition of titanium alkoxide to acetic acid in butan-1-ol was shown to increase the pH until a limiting value was reached, see Figs. (2.2) and (2.3). The possible reason for this will be discussed later. From the pH curves at varying titanium alkoxide and acetic acid concentrations a suitable titration end-point was determined and a limiting titanium alkoxide concentration was defined, beyond which the results would be subject to errors greater than 5 per cent. A list of the pH end-point values for each titanium alkoxide in butan-1-ol with acetic
Fig. (2.1) The effect of Ti(OCBu)₄ addition on the neutralisation plot of acetic acid \( \sim (0.10M) \) in butan-1-ol (5 cm³).

Volume of Potassium Methoxide (0.05M) in ml:

- ○ 0 µl of Ti(OCBu)₄
- ▲ 10 µl of Ti(OCBu)₄
- □ 40 µl of Ti(OCBu)₄
Fig. (2.2) The effect on pH of Ti(0Bu)$_4$ addition to acetic acid (0.10M) in butan-1-ol (10 cm$^3$)

* Ti(0Bu)$_4$, 25$\mu$l = 0.0147M
Fig. (2.3) The effect of TiTE addition to acetic acid (0.10M) in butan-1-ol.

* TiTE, 25 μl = 0.0147M
acid is given in Table (2.4). For TiTE, with substituted benzoic and acetic acids, an end-point of 9.6 pH units was found to be satisfactory for the standard conditions quoted.

(2.2.2) The Thermostats

Two thermostats were used in this investigation. The heating control unit on the first thermostat was lent by B.P. Chemicals International Limited. This thermostat was accurate to ± 0.2°C. The second thermostat, which supplemented the first at a later stage, was made in the Chemistry Department. This thermostat had a voltage reduction of 240 volts to 50 volts. The bath contained Synperonic NX high temperature detergent, which was heated by a one kilowatt AC heater, the detergent being stirred by a ¼ h.p. motor and paddle. Two contact thermometers were mounted in the bath, one being a simple switching thermometer, and the other being part of a safety cut-out system, see Fig. (2.4). The complex nature of the thermostat was necessary because of the requirements of the Health and Safety at Work Act. This thermostat was accurate to ± 0.1°C.

<table>
<thead>
<tr>
<th>Concentration m</th>
<th>pH at end-point for Acetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(OC_{2}H_{5})_{4}</td>
<td>0.020</td>
</tr>
<tr>
<td>Ti(iPrO)_{4}</td>
<td>0.020</td>
</tr>
<tr>
<td>Ti(OC_{4}H_{9})_{4}</td>
<td>0.020</td>
</tr>
<tr>
<td>TiTE</td>
<td>0.030</td>
</tr>
<tr>
<td>Ti Acac</td>
<td>0.030</td>
</tr>
</tbody>
</table>

(2.2.3) Experimental Procedure

Reaction mixtures were prepared by using Grade A volumetric apparatus. Sufficient titanium alkoxide, to give 50.00 cm$^3$ of a 0.02M solution, was weighed into a 50.00 cm$^3$ graduated flask. To this, 20.00 cm$^3$ of butan-1-ol was added and thoroughly mixed to avoid direct contact between catalyst and
the carboxylic acid added next. Sufficient carboxylic acid, to give 50 cm.³ of a 0.10M solution, was weighed into the 50.00 cm.³ graduated flask and butan-1-ol was added to give a total volume of 50.00 cm.³. After thorough mixing, 5.00 cm.³ portions of the reaction mixture were pipetted into 10.00 cm.³ capacity spring-loaded clear-seal tubes; see Fig. (2.5). Eight tubes containing the reaction mixture were placed in the thermostat. As each sample was removed at a given time, it was immediately immersed in cold water to prevent further reaction.

The contents of each reaction tube were titrated potentiometrically, with potassium methoxide (0.05M in a 10.00 cm.³ burette) to determine the residual acid. The contents of the reaction tube were poured into a 25 cm.³ beaker; the tube was washed with two 5 cm.³ portions of butan-1-ol and the washings were added to the beaker. The electrodes of the pH meter were placed in the beaker and the contents were stirred by means of a Gallenkamp magnetic stirrer. The pH meter was set for automatic titration with the burette tap half open. The proportional band was set to 1.5 pH units below the predetermined end-point cut-out value, so that only small additions of titrant were added as the end-point of the reaction mixture was approached.

The sample used for analysis to determine the initial point in the reaction versus time curve for reactions involving TiTE, was a 5.00 cm.³ portion taken directly from the graduated flask containing the reaction mixture. However for reactions involving titanium tetra-n-butoxide the initial point was taken from the analysis of a mixture which had been in the thermostat for 5 mins.; this is the time taken for the contents of the tube to reach the thermostat temperature. The reason for taking the initial point after 5 mins. for reactions involving titanium tetra-n-butoxide, was that a significant drop in titre occurred in this five minute warming-up period, whereas there was no significant change in the first 5 mins. for reactions involving TiTE.

The reaction tubes were removed from the thermostat at approximately equal intervals to cover between 65 and 70% of the reaction under consideration.
A Reaction Tube.
When the initial rate of a reaction was required most of the reaction tubes were removed during the first 20% of reaction in order to obtain a greater degree of accuracy from the first part of the reaction versus time curve. For experiments to show that reactions were going to completion, some reaction tubes remained in the thermostat until as much of the reaction as practically possible had occurred.

A number of reactions were studied in 10.0 cm.³ capacity sealed glass tubes (fusion under nitrogen). This was necessary for slow reactions, when samples were in the thermostat for a long time and leakage of reactants through the glass clear-seal stoppers could produce significant errors. The occurrence of leakage was however very rare. Experiments to determine the 'spontaneous rate' were undertaken for carboxylic acids which were esterified appreciably with butan-1-ol in the absence of a titanium alkoxide. The procedure for preparing these reaction solutions was as before but with the omission of titanium alkoxide.

(2.3) Product Analysis

(2.3.1) Infra-red Spectroscopy

To show that the disappearance of acid from a mixture of butan-1-ol, a carboxylic acid and titanium alkoxide was due to the formation of butyl ester and not due to the acid undergoing some reaction with the titanium alkoxide, infra-red spectroscopy was employed. Reference samples of butyl acetate in carbon tetrachloride and butyl acetate with acetic acid in carbon tetrachloride were submitted for infra-red analysis. The butyl ester peak appeared at 1737 cm⁻¹ and the acetic acid peak at 1713 cm⁻¹. Reaction samples, after various periods of reaction time, were extracted with carbon tetrachloride. The infra-red spectra of these showed that the disappearance of the acid peak at 1713 cm⁻¹ corresponded quantitatively to the formation of the ester peak at 1737 cm⁻¹. This was observed for TiTE and titanium tetra-n-butoxide catalysts, which are the two main catalysts under consideration in this study.
(2.3.2) Colorimetric Analysis

Titanium salts in a sulphuric acid medium give an orange-yellow colour with hydrogen peroxide. The nature of the coloured product has not been established. This coloration conforms to Beer's Law under certain conditions. To determine the nature and purity of titanium compounds used or produced in this investigation, it was necessary to make a calibration graph by using a standard titanium compound; potassium titanyl oxalate $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ was selected. A gravimetric analysis of this compound showed it to be 99 per cent pure.

A 0.01 M solution of potassium titanyl oxalate in sulphuric acid (1.0 M) was prepared in a 1 l. graduated flask. Care was taken to ensure that any carbon dioxide evolved was removed before the flask was filled to the mark. Aliquots of this solution were taken and contained 0.1-2.0 mg. of titanium; each aliquot was pipetted into a 100 cm.$^3$ graduated flask and 1.0 M sulphuric acid (90 cm.$^3$) and 10 volume hydrogen peroxide (1.0 cm.$^3$) were added. The solution was made up to the mark with distilled water. Optical density measurements were made on the contents of each flask by using a Unicam SP 600 Spectrophotometer. A pair of matched 4.0 cm. glass cells were used at a wavelength of 410 nm. This gave the calibration graph Fig. (2.6).

By using this technique the formula weight per titanium atom of unknown titanium compounds could be determined and also the purity of titanium compounds of known molecular weight. See Table (2.3).

(2.4) Molecular Weight Determination by the Lowering of the Vapour Pressure

Dissolving a non-volatile solute in a liquid produces a lowering of vapour pressure. From this depression in vapour pressure it is possible to determine the molecular weight of a given solute. By using the apparatus and method described by A.W.C. Menzies, see Fig. (2.7), the molecular form taken by titanium alkoxides in ethanol was determined. This technique proved unsuitable for butan-l-ol (b.p. 117°C) because of heat insulation problems, whereas for ethanol (b.p. 78°C) it was possible to obtain consistent results.
Fig. (2.6) Calibration graph for titanium determination on the spectrophotometer.

mg. of Titanium per 100 cm$^3$ of solution.
Menzies' Apparatus

Fig 2.7
The apparatus employed enables measurement of the depression of vapour pressure at the b.p. of the solvent, which is much greater than that at room temperature, and the solution acts as its own manometric liquid.

It was first necessary to calibrate the apparatus for a compound of known molecular weight, in this case naphthalene. The bulb of the outer jacket was charged two-thirds full with ethanol, the empty "test-tube" replaced in position, and the ethanol boiled in an isomantle for ten minutes under its reflux condenser, in order to expel dissolved gases. The isomantle was removed, the test tube taken out, charged two-thirds full with boiled-out ethanol from the jacket, and replaced in position with its stopper left out. The ethanol in the jacket was again boiled for a minute to expel air, after which the tap was closed sufficiently to cause a vigorous bubbling of vapour through the liquid in the test tube. After this blowing-through process had continued for two or three mins. the stopper was warmed up by inserting it obliquely in position. The escaping vapour condensed to form several drops around the stopper. The stopper was then pushed home and at the same time the tap was opened. The liquid above the stopper made the joint gas-tight. The apparatus was then allowed to stand for a few minutes until the temperature of the inner tube adjusted itself to the true b.p. of the ethanol. The reading of the difference in levels between the gauge tube and the inner jacket caused by capillarity was then taken, this being the zero reading. On removing the stopper, portions of solute of known weight could be added. Solution was assisted by blowing vapour through from the outer jacket by closing the tap, after which the tap was opened and the stopper was again inserted exactly as before. The apparatus was shaken periodically to prevent abnormal concentrations forming and also to cool down the inner jacket. When the level in the gauge remained constant a reading was taken and corrected by use of the zero reading. The stopper was then removed, after the ethanol around the joint had been removed by a filter paper and the volume in the test tube was noted.
The molecular weight of the solute was then calculated by using the following equation

\[ M = \frac{1000 \times W \times K \times B}{L \times V \times 760} \]  

(2.1)

W = weight of solute in grams.
B = barometric height in mmHg.
L = measured lowering of pressure in mm.
V = volume of the solution in cm\(^3\)
K = the density of the solvent at its boiling point, which for ethanol is 871.5 mg./cm\(^3\).

The results of the molecular weight determinations for titanium tetra-n-butoxide and TiTE in ethanol are given in Table (2.5)

<table>
<thead>
<tr>
<th>Molarity of solute</th>
<th>Molecular weight</th>
<th>Degree of association</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0025M TiTE</td>
<td>430 ± 15</td>
<td>0.93</td>
</tr>
<tr>
<td>0.0059M TiTE</td>
<td>780 ± 18</td>
<td>1.69</td>
</tr>
<tr>
<td>0.0221M TiTE</td>
<td>795 ± 13</td>
<td>1.72</td>
</tr>
<tr>
<td>0.0176M Ti(OC6H13)</td>
<td>930 ± 22</td>
<td>2.74</td>
</tr>
</tbody>
</table>

\[ \text{Based on pure monomer neglecting residual alcohol} \]
EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Bis (Triethanolamine) Titanium Di-Isopropoxide (TiTE)

Esterification of acetic acid with butan-1-ol in the presence of TiTE at 110°C was studied in detail initially to determine the kinetics of the reactions in the system. For a given experiment it was shown by inspection that the log (potassium methoxide titre) versus time plot gave a satisfactorily straight line up to 60-70 per cent reaction, see Figs. (3.1) - (3.3). The reaction was therefore considered to be first order in acetic acid; this was also observed for benzoic acid, see Fig. (3.4). In the results in Table (3.1) first-order rate constants $k_1$ are quoted under the given conditions. The initial rates (i.e. at $t = 0$), determined from $k_1$ values, are also given; these are used in the discussion of results - see page 59.

From experiments at various concentrations of catalyst it was also found that the reaction was approximately first order in TiTE, see page 59. The apparent second-order rate constants $k_2^A$ are also given in Table (3.1). Having once determined the kinetics of this reaction it is not necessary to give both first-order rate constants and rates at $t = 0$ in most subsequent Tables. The TiTE concentrations used in calculating $k_2^A$ values are based on TiTE material as weighed out and the theoretical molecular weight, i.e. no allowance is made for results of purity determination, see page 33. All rates are determined by least squares analysis and the errors quoted are standard deviations.

(3.1.1) The Infra-Red Spectra of Species Present in the TiTE, Butan-1-ol and Acetic Acid System

The infra-red spectra of the components of this system were studied in the solvents carbon tetrachloride or chloroform, depending on their solubility in these solvents. A spectrum of 0.02M acetic acid shows bands at 1713 cm$^{-1}$ and 1290 cm$^{-1}$ which are characteristic wavelengths for $C=O$ and $C-O$ in the carboxylic acid dimer. However when 0.02M TiTE are present there is a considerable reduction in these peaks and the appearance of a broad peak at 1560 cm$^{-1}$ which indicates the presence of acetate ions. The presence of 0.05M butan-1-ol has no effect on the relevant peaks.
The spectra of a reaction mixture containing 0.02M TiTE and 0.1M acetic acid in butan-1-ol at 110°C were taken after various times between 0 and 420 mins. The spectra showed an increase with reaction time in the peak at 1730 cm\(^{-1}\), which corresponds to the signal for butyl acetate.
Fig. (3.1) First order rate plot for acetic acid 0.10M and TiTE 0.02M in butan-1-ol at 110°C
Fig. (3.2) First order rate plot for acetic acid $0.10\text{M}$ and TiTE $0.01\text{M}$ in butan-1-ol at $110^\circ\text{C}$.
Fig. (3.3) First order rate plot for acetic acid (0.05M) and TiTE (0.02M) in butan-1-ol at 110°C.
Fig. (3.4) First order rate plot for benzoic acid (0.10M) and TiTE (0.02M) in butan-1-ol at 10 °C.
### TABLE (3.1)

Esterification of Acetic Acid with Butan-1-ol at 110°C with TiTE as Catalyst

<table>
<thead>
<tr>
<th>Acetic Acid, M</th>
<th>TiTE, M</th>
<th>Rate at t = 0 x 10^5 mol l^-1 min.^-1</th>
<th>k_1 x 10^4 min.^-1</th>
<th>k_2A x 10^2 1 mol^-1 min.^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0500</td>
<td>0.0200</td>
<td>20.8 ± 0.7</td>
<td>41.7 ± 1.3</td>
<td>2.08 ± 0.07</td>
</tr>
<tr>
<td>0.0750</td>
<td>0.0200</td>
<td>34.5 ± 1.2</td>
<td>46.0 ± 1.6</td>
<td>2.30 ± 0.08</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0200</td>
<td>46.3 ± 1.8</td>
<td>46.3 ± 1.8</td>
<td>2.31 ± 0.09</td>
</tr>
<tr>
<td>0.1500</td>
<td>0.0200</td>
<td>67.7 ± 2.4</td>
<td>45.1 ± 1.6</td>
<td>2.26 ± 0.08</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0025</td>
<td>9.20 ± 0.4</td>
<td>9.20 ± 0.4</td>
<td>3.68 ± 0.16</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0050</td>
<td>14.6 ± 0.6</td>
<td>14.6 ± 0.6</td>
<td>2.92 ± 0.12</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0100</td>
<td>24.7 ± 0.0</td>
<td>24.7 ± 0.0</td>
<td>2.47 ± 0.00</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0150</td>
<td>35.1 ± 0.3</td>
<td>35.1 ± 0.3</td>
<td>2.34 ± 0.02</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0250</td>
<td>55.1 ± 0.2</td>
<td>55.1 ± 0.2</td>
<td>2.20 ± 0.01</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0200</td>
<td>42.9 ± 1.9</td>
<td>42.9 ± 1.9</td>
<td>2.15 ± 0.09</td>
</tr>
</tbody>
</table>

TiTE refluxed in butan-1-ol for two hours before the experiment.

### TABLE (3.2)

Esterification of Butan-1-ol at various concentrations of Acetic Acid and TiTE at 80°C

<table>
<thead>
<tr>
<th>Acetic Acid, M</th>
<th>TiTE, M</th>
<th>Rate at t = 0 x 10^5 mol l^-1 min.^-1</th>
<th>k_2A x 10^2 1 mol^-1 min.^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.0100</td>
<td>4.40 ± 0.03</td>
<td>4.40 ± 0.03</td>
</tr>
<tr>
<td>0.100</td>
<td>0.0150</td>
<td>6.01 ± 0.08</td>
<td>4.01 ± 0.06</td>
</tr>
<tr>
<td>0.100</td>
<td>0.0200</td>
<td>7.24 ± 0.14</td>
<td>3.62 ± 0.07</td>
</tr>
<tr>
<td>0.050</td>
<td>0.0200</td>
<td>3.86 ± 0.10</td>
<td>3.86 ± 0.10</td>
</tr>
<tr>
<td>0.150</td>
<td>0.0200</td>
<td>10.8 ± 0.03</td>
<td>3.61 ± 0.13</td>
</tr>
</tbody>
</table>
TABLE (3.3)

Esterification of Butan-1-ol with Acetic Acid (0.100 M) in the Presence of TiTE (0.020 M) at 80, 90, 100, 110 and 120°C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$k_2 A \times 10^2$ $\text{l mol}^{-1} \text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>3.62 ± 0.07</td>
</tr>
<tr>
<td>90</td>
<td>7.4 ± 0.00</td>
</tr>
<tr>
<td>100</td>
<td>13.7 ± 0.10</td>
</tr>
<tr>
<td>110</td>
<td>23.2 ± 0.90</td>
</tr>
<tr>
<td>120</td>
<td>36.4 ± 0.50</td>
</tr>
</tbody>
</table>

I Two identical results

TABLE (3.4)

Esterification of Butan-1-ol with Acetic Acid (0.100 M) in the Presence of TiTE (0.020 M) at 110°C with various amounts of water present

<table>
<thead>
<tr>
<th>Water, M</th>
<th>$k_2 A \times 10$ $\text{l mol}^{-1} \text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>2.32 ± 0.09</td>
</tr>
<tr>
<td>0.010</td>
<td>2.22 ± 0.11</td>
</tr>
<tr>
<td>0.040</td>
<td>2.30 ± 0.08</td>
</tr>
<tr>
<td>0.084</td>
<td>2.19 ± 0.07</td>
</tr>
</tbody>
</table>

The molarity of water quoted in this Table does not include traces of water present in the starting materials.
TABLE (3.5)

Esterification of Butan-1-ol with Acetic Acid (0.100 M) in the Presence of TiTE (0.020 M) with Potassium Acetate and Potassium Trifluoroacetate at 110°C

<table>
<thead>
<tr>
<th>Potassium Acetate, M</th>
<th>Potassium Trifluoroacetate, M</th>
<th>$k_{2A} \times 10^{-1}$</th>
<th>$\text{mol}^{-1} \text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.0000</td>
<td>2.32 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>0.0250</td>
<td>0.0000</td>
<td>2.78 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.0500</td>
<td>0.0000</td>
<td>2.91 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>0.0750</td>
<td>0.0000</td>
<td>3.23 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>0.1000</td>
<td>0.0000</td>
<td>3.51 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>0.1250</td>
<td>0.0000</td>
<td>3.61 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.0650</td>
<td>2.35 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.1310</td>
<td>2.27 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>± 0.0000</td>
<td>0.0000</td>
<td>2.14 ± 0.16</td>
<td></td>
</tr>
</tbody>
</table>

± 0.1 M in triethanolamine

TABLE (3.6)

Esterification of Acetic Acid (0.01 M) with Butan-1-ol at 110°C in the Absence of TiTE

<table>
<thead>
<tr>
<th>Reaction Time min.</th>
<th>Titre 0.05 M - Potassium Methoxide versus 5 cm$^3$ Portion of Reaction Mixture cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.01</td>
</tr>
<tr>
<td>20</td>
<td>9.98</td>
</tr>
<tr>
<td>50</td>
<td>9.99</td>
</tr>
<tr>
<td>100</td>
<td>9.97</td>
</tr>
<tr>
<td>150</td>
<td>9.98</td>
</tr>
<tr>
<td>200</td>
<td>9.96</td>
</tr>
<tr>
<td>400</td>
<td>9.97</td>
</tr>
</tbody>
</table>
TABLE (3.7)

Esterification of Butan-1-ol with some Substituted Acetic Acids (0.100 M) in the Presence of TiTE (0.020 M) at 110°C.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$k_2A \times 10^{1 \text{ mol}^{-1} \text{ min}^{-1}}$</th>
<th>$\sigma^*$</th>
<th>$E_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>2.32 ± 0.09</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2-Methylpropionic</td>
<td>2.05 ± 0.09</td>
<td>-0.190</td>
<td>-0.470</td>
</tr>
<tr>
<td>Propionic</td>
<td>2.54 ± 0.02</td>
<td>-0.100</td>
<td>-0.070</td>
</tr>
<tr>
<td>2,2-Dimethylpropionic</td>
<td>1.12 ± 0.03</td>
<td>-0.300</td>
<td>-1.540</td>
</tr>
<tr>
<td>Phenylacetic</td>
<td>4.20 ± 0.13</td>
<td>0.215</td>
<td>-0.380</td>
</tr>
<tr>
<td>3-Chloropropionic</td>
<td>3.55 ± 0.04</td>
<td>0.385</td>
<td>-0.900</td>
</tr>
<tr>
<td>2-Phenylpropionic</td>
<td>1.46 ± 0.01</td>
<td>0.110</td>
<td>-1.190</td>
</tr>
<tr>
<td>Phenoxyacetic</td>
<td>12.9 ± 0.20</td>
<td>0.850</td>
<td>-0.330</td>
</tr>
<tr>
<td>Monochloroacetic</td>
<td>24.8 ± 0.40</td>
<td>1.050</td>
<td>-0.240</td>
</tr>
</tbody>
</table>

Note

$\sigma^*$ - polar substituent constant

$E_s$ - steric substituent constant

TABLE (3.8)

Esterification of Substituted Acetic Acids (0.1 M) which show a Spontaneous Reaction

<table>
<thead>
<tr>
<th>Acid</th>
<th>Rate at $t = 0 \times 10^3$ mol $1^{-1} \text{ min}^{-1}$ with TiTE (0.020 M)</th>
<th>Rate at $t = 0 \times 10^4$ mol $1^{-1} \text{ min}^{-1}$ without TiTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenoxyacetic</td>
<td>2.59 ± 0.04</td>
<td>6.86 ± 0.06</td>
</tr>
<tr>
<td>Monochloroacetic</td>
<td>4.96 ± 0.09</td>
<td>2.37 ± 0.08</td>
</tr>
</tbody>
</table>
### TABLE (3.9)

Esterification of Butan-1-ol with some Meta- and Para-
Substituted Benzoic Acids (0.100 M) in the Presence of
TiTE (0.020 M) at 110°C

<table>
<thead>
<tr>
<th>Acid</th>
<th>Hammett Substituent Constant</th>
<th>$k_2^A \times 10^2$ l mol$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic</td>
<td>0.00</td>
<td>$3.52 \pm 0.09$</td>
</tr>
<tr>
<td>p-Methoxybenzoic</td>
<td>-0.27</td>
<td>$1.66 \pm 0.13$</td>
</tr>
<tr>
<td>p-Nitrobenzoic</td>
<td>0.78</td>
<td>$18.5 \pm 0.09$</td>
</tr>
<tr>
<td>p-Fluorobenzoic</td>
<td>0.06</td>
<td>$4.32 \pm 0.30$</td>
</tr>
<tr>
<td>p-Toluic</td>
<td>-0.17</td>
<td>$2.69 \pm 0.12$</td>
</tr>
<tr>
<td>p-Chlorobenzoic</td>
<td>0.23</td>
<td>$6.1 \pm 0.01$</td>
</tr>
<tr>
<td>m-Bromobenzoic</td>
<td>0.39</td>
<td>$8.6 \pm 0.06$</td>
</tr>
<tr>
<td>m-Toluic</td>
<td>-0.07</td>
<td>$3.22 \pm 0.23$</td>
</tr>
<tr>
<td>m-Nitrobenzoic</td>
<td>0.71</td>
<td>$15.5 \pm 0.04$</td>
</tr>
</tbody>
</table>

### TABLE (3.10)

Esterification of Some Ortho-Substituted Benzoic Acids (0.100 M)
with Butan-1-ol in the Presence of TiTE (0.020 M) at 110°C

<table>
<thead>
<tr>
<th>Acid</th>
<th>$k_2^A \times 10^2$ l mol$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic</td>
<td>$3.52 \pm 0.09$</td>
</tr>
<tr>
<td>o-Bromobenzoic</td>
<td>$4.57 \pm 0.05$</td>
</tr>
<tr>
<td>o-Toluic</td>
<td>$1.47 \pm 0.13$</td>
</tr>
<tr>
<td>o-Nitrobenzoic</td>
<td>$2.8 \pm 0.02$</td>
</tr>
<tr>
<td>o-Chlorobenzoic</td>
<td>$5.95 \pm 0.05$</td>
</tr>
</tbody>
</table>
For fixed TiTE concentration and a threefold variation in acetic acid concentration, the first-order rate constant, $k_1$, varied by less than 14 per cent, see Table (3.1). This variation is almost totally accounted for by the low $k_1$ value obtained for 0.05M acetic acid. The double log plot of rate at $t = 0$ versus acetic acid concentration for TiTE (0.02M) gave a line of gradient 1.05 ± 0.03, which is equal to $n$, the order of reaction with respect to acetic acid, see Fig. (3.5). The plot of initial rate versus acetic acid concentration for TiTE (0.02M) shows satisfactory rectilinearity and passes through the origin, see Fig. (3.6); there appears to be no systematic deviation.

The plot of initial rate versus TiTE concentration for a fixed acetic acid concentration (0.10M) shows that the experimental points lie on a straight line, see Fig. (3.7) but this straight line does not pass through the origin. This might suggest that there is a 'spontaneous reaction' under these conditions. If the line in Fig. (3.7) is extrapolated to the vertical axis an initial rate value of $4.5 \times 10^{-5}$ mol·l$^{-1}$·min$^{-1}$ is obtained, which represents a titre of 9.20 cm$^3$ after 400 minutes of reaction in the absence of TiTE. However the value observed for such a reaction is 9.97 cm$^3$ compared with an initial value of 10.00 cm$^3$, see Table (3.6), which allowing for experimental error, shows there to be no 'spontaneous reaction'. The double log plot of rate at $t = 0$ versus TiTE concentration for acetic acid (0.10M) gave a value of $n$, the order of reaction of 0.79 ± 0.05, see Fig. (3.8). This shows that there is an approximate conformity to first order behaviour in TiTE at concentrations of 0.0025M and greater. The most likely reason for the initial rate plot curving down to the origin at low TiTE concentration is that two different catalyst species are present. At low TiTE concentrations the catalyst will be in its monomeric form.
Fig. (3.5) Double log plot of log rate at \( t = 0 \) versus log Acetic Acid with TiTE (0.02M) in butan-1-ol at 110°C to determine the order of reaction, \( n \), with respect to acetic acid.
Fig. (3.6) Plot of Variation of rate at $t = 0$ versus acetic acid concentration with TiTE (0.02 M) in butan-1-ol at 110°C.
Fig. (3.7) Plot of variation of rate at $t = 0$ versus TiTE concentration with acetic acid (0.10M) in butan-1-ol at 110°C.
Fig. (3.8) Double log plot of log rate at \( t = 0 \) versus log TiTE with acetic acid (0.10M) in butan-1-ol at 110°C to determine the order of reaction, \( n \), with respect to TiTE.
N.B. The labile isopropoxy ligand will have undergone exchange with butan-1-ol.

At higher concentrations, titanates tend to form intermolecular coordinate linkages between the oxygen atoms of the alkoxy groups and titanium atoms, of the type shown in Fig (3.10)

This species will be less reactive than the former due to the coordinative bonding of the labile butoxy group. The TiTE may also be partially polymerised through alcoholysis.

The results obtained for the TiTE system were used to determine the apparent second order rate constant, \( k_2^A \). It was important that comparable conditions were used for determining \( k_2^A \) values, as a 2.5 fold increase in TiTE concentration brought about a systematic change in \( k_2^A \) by up to ca. 15%.

The results found after heating TiTE (0.02 M) in butan-1-ol at the b.p. for 2 h. before adding acetic acid (0.10 M), see Table (3.1) show that although there may have been some slight reduction in catalytic activity as measured by \( k_2^A \), this scarcely exceeds experimental error.
The kinetics of the reaction system were checked briefly at 80°C, see Table (3.2), to see whether there was any significant change in behaviour. The results show that the first-order behaviour in acetic acid is not quite as precise as for the system at 110°C. There is a 15% change in $k_2^A$ values for a threefold change in acetic acid concentration. The double log plot of initial rate versus acetic acid concentration, see Fig. (3.11), gives an order of reaction of ca. 0.9 in acetic acid. The TiTE kinetic behaviour at 80°C is closer to the behaviour of TiTE at 110°C, with the double log plot of initial rate versus TiTE concentration, see Fig. (3.12), giving an order of reaction about 0.72 in TiTE. From this fragmentary study at 80°C it was concluded that the kinetic behaviour of the system at 80°C was effectively the same as that at 110°C.

(3.1.3) The Effect of Water on the Kinetics of the Reactions in Acetic Acid, Butan-1-ol and TiTE System at 110°C

The values of $k_2^A$ see Table (3.4) are relatively unaffected for various concentrations of water. TiTE was not readily hydrolysed in the presence of water at 110°C. The resistance to hydrolysis of TiTE is probably due to the presence of the chelate triethanolamine ligands, which hinder sterically the attack of water molecules, as well as giving the titanium atom its stable octahedral coordination.

(3.1.4) The Activation Energy of the Reaction in the Acetic Acid, Butan-1-ol and TiTE System.

The apparent second-order rate constant, $k_2^A$, was determined for a standard reaction mixture at 10°C intervals over the temperature range of 80-120°C, see Table (3.3). The activation energy was determined from the plot of $\log k_2^A$ versus reciprocal temperature see Fig. (3.13) and found to be $16.3 \pm 0.3$ kcal mole$^{-1}$ by least squares analysis of the results; $\log A$ is $9.68 \pm 0.3$ with $A$ in litres mol$^{-1}$ min$^{-1}$. Many reactions in solution have an $A$ value in the region of $10^{10} - 10^{13}$ l mol$^{-1}$ min$^{-1}$. This value will not be discussed further because of the complex nature of the $k_2^A$ values.
Fig. (3.11) Double log plot of log rate at $t = 0$ versus log acetic acid with TiTE (0.02M) in butan-1-ol at 80°C to determine the order of reaction, $n$, with respect to acetic acid.
Fig. (3.12) Double log plot of log Rate at t = 0 versus log TiTE with acetic acid (0.10M) in butan-1-ol at 80°C to determine the order of reaction, n, with respect to TiTE.
Fig. (3.13) Arrhenius plot for TiTE (0.02M) and acetic acid (0.10M) in butan-1-ol.
(3.1) Suggested Mechanism to Explain the Kinetics for the

TiTE System

The two forms of TiTE already suggested in section (3.1.2) will give rise
to different rate constants for the esterification of acetic acid and butan-1-ol.
The proposed dimer structure has coordinate bonding of the labile butoxy groups
and will be therefore less reactive than monomeric TiTE. A mathematical
treatment of the rates of reaction for these two catalyst species was undertaken
to reproduce reaction rates for a given catalyst concentration which agreed closely
with those observed for a given set of conditions.

Consider the following equations

\[
\frac{K_{21}}{2} \text{Ti} \left(\text{OBu}\right)_{2}(\text{TR})_{2} \rightleftharpoons \text{Ti} \left(\text{OBu}\right)_{2}(\text{TR})_{2} \tag{3.1}
\]

\[
\text{Ti} \left(\text{OBu}\right)_{2}(\text{TR})_{2} + \text{AcOH} \xrightarrow{K_{1}} \text{Ti(OBu)(OAc)(TR)}_{2} + \text{BuOH} \tag{3.2}
\]

\[
\text{Ti(OBu)(OAc)(TR)}_{2} \xrightarrow{K_{1}} \text{TiO(TR)}_{2} + \text{AcOBu} \tag{3.3}
\]

\[
\frac{K_{2}}{2} \left(\text{Ti(OBu)(TR)}_{2} + \text{AcOH} \xrightarrow{K_{2}} \text{Ti(OBu)(OAc)(TR)}_{2} \cdot \text{Ti(OBu)}_{2}(\text{TR})_{2} + \text{BuOH} \tag{3.4}
\]

\[
\text{Ti(OBu)(OAc)(TR)}_{2} \cdot \text{Ti(OBu)(TR)}_{2} \xrightarrow{K_{2}} \text{TiO(TR)}_{2} \text{Ti(OBu)}_{2}(\text{TR})_{2}
\]

\[
\text{TiO(TR)}_{2} + 2\text{BuOH} \rightarrow \text{Ti(OBu)}_{2}(\text{TR})_{2} + \text{H}_{2}\text{O} \tag{3.6}
\]

\[
\text{TiO(TR)}_{2} \text{Ti(OBu)}_{2}(\text{TR})_{2} + 2\text{BuOH} \rightarrow \left(\text{Ti(OBu)}_{2}(\text{TR})_{2}\right)_{2} + \text{H}_{2}\text{O} \tag{3.7}
\]

TR = Triethanolamine anion
Ac = CH\text{$_{3}$}CO
Bu = CH\text{$_{3}$}(\text{CH\text{$_{2}$})$_{3}$}

Let the total Ti concentration be C moles of monomer/l.
Then
\[
\left[\text{Ti(OBu)}_2\text{(TR)}_2\right] = \frac{1}{2}(C - \left[\text{Ti(OBu)}_2\text{(TR)}_2\right]) \quad (3.8)
\]
and
\[
K_{21} = \frac{\left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2}{\left[\frac{1}{2}(C - \left[\text{Ti(OBu)}_2\text{(TR)}_2\right])\right]^2} \quad (3.9)
\]
Therefore
\[
K_{21} = \frac{\left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2}{\frac{1}{2}(C - \left[\text{Ti(OBu)}_2\text{(TR)}_2\right])^2} \quad (3.10)
\]
Therefore
\[
2\left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2 = K_{21} C - K_{21} \left[\text{Ti(OBu)}_2\text{(TR)}_2\right] \quad (3.11)
\]
Therefore
\[
2\left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2 + K_{21} \left[\text{Ti(OBu)}_2\text{(TR)}_2\right] = K_{21} C = 0 \quad (3.12)
\]
Solving the quadratic equation, we have
\[
\left[\text{Ti(OBu)}_2\text{(TR)}_2\right] = \frac{-K_{21} \pm \sqrt{K_{21}^2 + 8K_{21}C}}{4} \quad (3.13)
\]
The rate of reaction = \( k \left( k_1 \left[\text{Ti(OBu)}_2\text{(TR)}_2\right] \left[\text{AcOH}\right] + k_2 \left[\text{Ti(OBu)}_2\text{(TR)}_2\right] \left[\text{AcOH}\right] \)
\[
\frac{k}{k_{\text{obs}}} = k_{\text{app}}^{\text{app}} \left[\text{AcOH}\right] C \quad (3.15)
\]
Therefore
\[
k_{\text{app}}^{\text{app}} = \frac{k_1 K_1 \left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2 + K_2 \left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2}{C K_{21} C} \quad (3.16)
\]
This can be represented as
\[
k_2 = \alpha \left[\text{Ti(OBu)}_2\text{(TR)}_2\right] + \beta \left[\text{Ti(OBu)}_2\text{(TR)}_2\right]^2 \quad (3.17)
\]
where \( \alpha = k_1 K_1 \) and \( \beta = \frac{k_2 K_2}{K_{21}} \).
This mathematical treatment can be used by guessing values of $\alpha$, $\beta$ and $k_{21}$ until a suitable match of the $k_2$ versus catalyst concentration curve is achieved.

The following values were found to give the closest value of the rate constant $k_2^A$ at various catalyst concentrations:

$$k_{21} = 0.001 \quad \alpha = 0.82 \quad \beta = 24.0$$

<table>
<thead>
<tr>
<th>Catalyst [M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0025</td>
</tr>
<tr>
<td>0.005</td>
</tr>
<tr>
<td>0.010</td>
</tr>
<tr>
<td>0.015</td>
</tr>
<tr>
<td>0.020</td>
</tr>
<tr>
<td>0.025</td>
</tr>
</tbody>
</table>

This proposed mechanism does not allow for the observations discussed in section (3.1.10) where protonation of the nitrogen atom of the TiTE monomer is discussed.

(3.1.6) The Effect of TiTE Concentration on the pH of Reaction Solutions.

Early experiments undertaken with a pH meter in the development of an analytical technique for the acetic acid and TiTE in butan-1-ol system, showed that the pH of solutions increased towards a limiting value when the TiTE concentration was increased, see Fig. (2.3). This effect was also observed when triethanolamine was added to butan-1-ol or $0.1\text{M}$ acetic acid in butan-1-ol, see Fig. (3.14). Together with the observation that 3, 5-dinitrobenzoic acid forms a salt with triethanolamine, see section (3.1.10), this suggests that the nitrogen atom of the triethanolamine molecule or ligand is capable of coordinating with a proton from either acetic acid or butan-1-ol. This may also explain the flattening of the pH versus base titrant curves with increasing
Fig. (3.14) Plot of pH versus additions of TiTE and triethanolamine to acetic acid (0.10M) in butan-1-ol.

Molarity of additive

- TiTE
- Triethanolamine
TiTE concentration discussed in section (2.2.1), see Fig. (2.1).

Similar observations to those mentioned above have also been made for the titanium tetrabutoxide catalyst system. This suggests that the TiTE or titanium tetrabutoxide may coordinate with protons through the butoxide group. However, the above observations may be due to some extent to the effects of the system on the behaviour of the glass electrode.

(3.1.7) The Effect of Addition of Potassium Acetate and of Triethanolamine to the Acetic Acid, Butan-1-ol and TiTE System

Evidence of acetate ion formation found in the i.r. spectroscopy of this system, (see page 48) suggested that acetate ions may play a part in the reaction mechanism. In order to show this, quantities of potassium acetate were added to the system, see Table (3.5.). The results show that the reaction rate constant $k_2^A$ is increased with increasing [potassium acetate], this increase only levelling off as the saturation point is reached, see Fig. (3.5.)

In order to establish whether the above acceleration was due to a 'salt effect', similar experiments were carried out with the salt of a strong acid and a strong base. Potassium trifluoroacetate was found to be a suitable salt. The results show that there was no 'salt effect', see Table (3.5.). A quantity of triethanolamine was also added to a standard reaction mixture and no significant change in the rate constant $k_2^A$ was observed, see Table (3.5.).

The increase in reaction rate with acetate ion addition may be due to the suppression of the formation of a less reactive catalytic species. This reaction could take the following form

$$\text{Ti(OBu)}_2(\text{TR})_2 + \text{AcOH} \rightarrow \text{Ti(OBu)}_2(\text{TR})\text{TRH}^+ + \text{OAc}^-$$

(3.18)
The presence of acetate ions would force the equilibrium to the left therefore increasing the concentration of the more active TiTE and hence increasing the rate. Another possible reaction scheme is as follows:

$$\text{Ti(OBu)}_2(\text{TR})_2 + \text{AcOH} \rightleftharpoons \text{Ti(OBu)HOBu}(\text{TR})_2 + \text{AcO}^- \quad (3.19)$$

In order to explain the increased reaction rates observed with the addition of acetate ions to the TiTE, acetic acid and butan-1-ol system a mathematical treatment has been undertaken based on equilibrium reactions of the system.

Consider the following reaction scheme

$$\text{Ti(OBu)}_2(\text{TR})_2 + \text{AcOH} \xrightarrow{K_1} \text{Ti(OBu)(OAc)(TR)}_2 + \text{BuOH} \quad (3.20)$$

$$\text{Ti(OBu)(OAc)(TR)}_2 \xrightarrow{K_1} \text{TiO}(\text{TR})_2 + \text{AcOBU} \quad (3.21)$$

$$\text{TiO}(\text{TR})_2 + 2\text{BuOH} \xrightarrow{\text{Fast}} \text{Ti(OBu)}_2(\text{TR})_2 + \text{H}_2\text{O} \quad (3.22)$$

$$\text{Ti(OBu)}_2(\text{TR})_2 + \text{AcOH} \xrightarrow{K'} \text{Ti(OBu)(HOBu)(TR)}_2 + \text{AcO}^- \quad (3.23)$$

The increased reaction rate caused by the addition of acetate ions could be explained by the displacement of the equilibrium in equation (3.23) where Ti(OBu)(HOBu)(TR)_2 is a less reactive catalyst than
Fig. (3.15) Plot to show the effect of acetate ions on the reaction rate constant for acetic acid (0.10M) and TiTE (0.02M) in butan-1-ol at 110°C.
Ti(OBu)$_2$(TR)$_2$.

Total catalyst concentration =

$$C_1 = [\text{Ti(OBu)}^+\text{(HOBu)}(\text{TR})_2] + [\text{Ti(OBu)}_2(\text{TR})_2]$$

(3.24)

$$K' = \frac{[\text{Ti(OBu)}^+\text{(HOBu)}(\text{TR})_2][\text{OAc}^-]}{[\text{Ti(OBu)}_2(\text{TR})_2][\text{AcOH}]}$$

(3.25)

$$K' = \frac{(C_1 - [\text{Ti(OBu)}_2(\text{TR})_2])}{[\text{Ti(OBu)}_2(\text{TR})_2][\text{AcOH}]} [\text{OAc}^-]$$

(3.26)

$$K' [\text{Ti(OBu)}_2(\text{TR})_2][\text{AcOH}] = C_1 [\text{OAc}^-] - [\text{Ti(OBu)}_2(\text{TR})_2][\text{OAc}^-]$$

(3.27)

$$[\text{Ti(OBu)}_2(\text{TR})_2](K' [\text{AcOH}] + [\text{OAc}^-]) = C_1 [\text{OAc}^-]$$

(3.28)

$$[\text{Ti(OBu)}_2(\text{TR})_2] = \frac{C_1 [\text{OAc}^-]}{K'[\text{AcOH}] + [\text{OAc}^-]}$$

(3.29)

$$\frac{1}{[\text{Ti(OBu)}_2(\text{TR})_2]} = \frac{1}{C_1} \left( \frac{K'[\text{AcOH}]}{[\text{OAc}^-]} + 1 \right)$$

(3.30)
Rate = \frac{k_1 k_2 c_1 [AcOH]}{K'[AcOH] + 1} \quad (3.31)

The [AcOH] will not be equal to the initial concentration [AcOH]_0, because of acetate ion formation, but since [AcOH]_0 > [TiTE], [AcOH] >> [OAc].

Since \[ k_a = \frac{[H^+] [OAc^-]}{[AcOH]} \] (3.32)

\[ K'[AcOH] = \frac{K'[H^+]}{K_a} \quad (3.33) \]

The observed limiting increase in \( k_2^* \) for potassium acetate addition is by a factor of 1.57, see fig. (3.15). If we consider a standard set of reaction conditions, then

\[ K_a = 10^{-9.2} \]

Taking \( K_a = 10^{-9.2} \) and estimating the 'real' pH = 8.1 (as opposed to the observed pH of 6.4)

\[ H^+ = 7.943 \times 10^{-9} \]

\[ K_a = \frac{[H^+] [OAc^-]}{[HOAc]} \]

\[ 6.31 \times 10^{-10} = 7.943 \times 10^{-9} \cdot \frac{[OAc^-]}{[HOAc]} \]

\[ \frac{[HOAc]}{[OAc]} = \frac{7.943 \times 10^{-9}}{6.31 \times 10^{-10}} = 12.588 \]
Also

\[ [H\ OAc] + [OAc^-] = 0.1 \]

and

\[ [H\ OAc] = 0.09264 \]

\[ [OAc^-] = 0.00736 \]

Assuming \[ [OAc^-] = [Ti(OBu)(HOBu)(TR)\_2] \]

\[ [Ti(OBu)(HOBu)(TR)\_2] = 0.00736 \]

\[ \therefore [Ti(OBu)\_2(TR)\_2] = 0.020-0.00736 = 0.01264 \]

\[ K = \frac{0.00736}{0.01264 \times 12.588} = 0.04626 \]

\[ K \frac{[AcOH]}{[OAc^-]} = 0.04626 \times 12.588 = 0.582 \]

This result agrees closely with the observed result. The value obtained from this calculation would be considerably changed by a slight variation in pH value. The pH was 'guessed' at 8.1 to obtain the correct factor for the limiting effect of OAc⁻ on the rate. Thus any observed pH value used in this calculation would have to be reliable which it has been shown not to be in this case. Had there been time for further study on the effect of acetate ions in this system more information could have been obtained by studying the effect of varying [catalyst] and [TiTE] at various [acetate ion]. Until this is done there seems little point in elaborating the mechanism by introducing into the scheme on page 64 the previously postulated monomer-dimer equilibrium for the TiTE catalyst.

(3.1.8) The Hammett Treatment of the Esterification of Some Meta- and Para-Substituted Benzoic Acids with Butan-1-ol in the Presence of TiTE Catalyst

In order to discover more about the mechanism of esterification with TiTE as catalyst, a range of meta- and para-substituted benzoic acids was employed so that a Hammett plot could be made. The rate constants for these systems
are given in Table (3.9). The resulting Hammett plot, fig. (3.16), shows that this is a satisfactory linear relationship between \( \log_{10} k^A_2 \) and the substituent constant, \( \sigma \). However there is one point which deviates significantly from this linearity, i.e. that for \( p \)-methoxybenzoic acid. The reaction constant, \( \rho \), was evaluated as 0.89 ± 0.02 by least squares analysis of the above data, with a correlation coefficient of 0.996 if the \( p \)-methoxybenzoic acid value is ignored. However, if the data for \( p \)-methoxybenzoic acid is included \( \rho \) is 0.93 with a correlation coefficient of 0.992 ± 0.03. This deviation for \( p \)-methoxybenzoic acid from the Hammett plot has also been observed by Habib and Malek. They attribute this to a mesomeric para-interaction of the methoxy group with the reaction site, which leads to a decrease in the acidity of the carboxy group of \( p \)-methoxybenzoic acid and to irregularity in the Hammett relation. To allow for such effects modifications of the Hammett treatment have been suggested by several workers but these will not now be considered. Since the Hammett equation is based on the ionisation of benzoic acids it is difficult to understand why the ordinary \( p \)-methoxybenzoic acid Hammett \( \sigma \) value is not applicable to this reaction. Perhaps this is because the \( \sigma \) value was based on the ionisation of substituted benzoic acids in water whereas the present study involves an anhydrous medium in butan-1-ol.

The \( \rho \) value of 0.89 shows that ease of esterification increases with acid strength. This value can be compared to \( \rho \) equal to -0.57 for the acid-catalysed esterification of substituted benzoic acids with methanol at 60°C. The catalyst used in that work was toluene - \( p \) - sulphonlic acid.

(3.1.9) The Esterification of Some Ortho-Substituted Benzoic Acids

with Butan-1-ol in the Presence of TiTE Catalyst

This system was studied in order to determine the effect of steric interactions of ortho-substituted groups on the apparent second-order rate constant, \( k^A_2 \), of esterification for substituted benzoic acids. The \( k^A_2 \) values that were obtained are in Table (3.10). The steric interaction of the
Fig. (3.16) Hammett plot for esterification of some meta and para substituted benzoic acids with TiTE (0.02M) in butan-1-ol at 110°C.
ortho-substituted benzoic acids must be considered together with difference in polar effects for ortho- and para-substitution.

The observed $k_2^A$ value for ortho-toluic acid was considerably smaller than that for para-toluic acid. This suggests that the steric hindrance of the methyl group plays a more important role in the reaction than the enhanced electron releasing effect of the ortho-methyl group.

The observed $k_2^A$ values for ortho-bromo- and ortho-chloro-benzoic acids are close to that for $p$-chlorobenzoic acid. This may indicate virtually no steric effect, with polar effects comparable as between ortho and para substitution or much more likely that some steric hindrance occurs from the chloro and bromo groups, which are about the same size as the methyl group, with a larger electron-attracting effect of the ortho substituents.

For ortho- and para-nitrobenzoic acid the $k_2^A$ value for the ortho acid was much smaller than that for $p$-nitrobenzoic acid and even smaller than for benzoic acid. It is obvious that steric hindrance is the dominant factor here because on a polar basis the nitro group should enhance the rate of esterification.

(3.1.10) Results Obtained in the Determination of the Structure of the Complexes formed between 3, 5-Dinitrobenzoic Acid and TlTE in Butan-1-ol.

(1) Preparation

Sufficient 3, 5-dinitrobenzoic acid (1.06 g.) was added to a 50 cm$^3$ graduated flask, to make a 0.10 M solution. To this butan-1-ol (20 cm$^3$) was added and then sufficient TlTE (0.4619 g.), to make a 0.02 M solution. This produced a dense white precipitate. After making the contents of the flask up to the mark with butan-1-ol the mixture was filtered at the pump and washed with 2 x 5.0 cm$^2$ portions of butan-1-ol.

(2) Analysis of the Complexes

The dry precipitate, I, weighed 0.580 g. On titrating a 5.0 cm$^3$ portion of the filtrate with potassium methoxide (0.05 M) a titre of ca. 7.5 cm$^3$ was
Fig (3.18.)

Benzene ring

-CH

-CH₂CH₂N

Solvent

TMS
obtained. This is to be compared to a 10.0 cm$^3$ titre for an equivalent solution without TiTE. The filtrate on being kept yielded a small quantity (0.23 g.) of a second precipitate, II, which was in the form of yellow needle-shaped crystals. After filtration a 5.0 cm$^3$ portion of this second filtrate gave a titre with potassium methoxide (0.05M) of ca. 6.0 cm$^3$. This suggests that every molecule of TiTE has taken up 2 molecules of acid.

Infra-red spectroscopy did not prove particularly helpful in determining the structures of I and II. However, it gave evidence of carboxylate formation in each case. Mass spectrometry failed to give any useful results for elucidating the structures of I and II.

NMR proved a more useful technique. The spectrum of complex I had a 'noisy' base line and did not give a clear picture of the structure of complex I, see Fig. (3.17). However on recrystallising complex I from butanone a much sharper spectrum was obtained, see Fig (3.18).

This spectrum showed that for each molecule of TiTE two molecules of acid were present and there was no evidence of the presence of labile butoxy or isopropoxy groups, suggesting the structure might be that shown in Fig (3.19).

![Figure 3.19](image)

However, it cannot be ruled out that the acid group may attack the nitrogen on the triethanolamine ligand to form a salt; this is because of the similarity between the spectrum observed and that of the spectrum of the salt produced by mixing triethanolamine and 3, 5-dinitrobenzoic acid in
Butan-1-ol. If this were true, the absence of butoxy or isopropoxy ligands would mean that the triethanolamine ligand had formed a chelate as suggested in Fig. (3.20)

![Figure (3.20)](image)

This structure seems unlikely on the grounds that it does not fit any likely mechanism for esterification on the evidence compiled so far.

The NMR spectrum of complex II gave a picture similar to that for complex I after recrystallisation from butanone.

Colorimetric analysis for the titanium content of the two complexes I and II was attempted. Solutions were made of known weight of complex in the manner described on p. 43. Complex I gave a formula weight value of 650 per Ti atom, which does not fit any likely structure for the compound. Complex II and complex I which had been recrystallised from butanone were both insoluble in suitable solvents and therefore this technique proved useless in these cases.

Carbon, nitrogen and hydrogen analysis of complexes I and II gave the results in Table (3.12).

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex I</td>
<td>37.7%</td>
<td>9.6%</td>
<td>3.6%</td>
</tr>
<tr>
<td>Complex II</td>
<td>43.15%</td>
<td>11.5%</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

Again a suitable structure for the initial complex I could not be suggested. For complex II the formula suggested in Fig (3.19) would have 40.73% carbon, 10.97% nitrogen, and 4.44% hydrogen which, allowing for traces of moisture would suggest Fig (3.19) as a likely structure.
(3.1.11) The Taft Treatment of the Reactions of Some Substituted Acetic Acids with Butan-1-ol in the Presence of TiTE Catalyst

Some selected substituted acetic acids were studied comparatively so that a Taft treatment might be undertaken for the TiTE catalyst system. There was insufficient time available to follow the full ideal range of substituted acetic acids. However, sufficient acids were studied to give some useful information on the importance of polarity and steric effects on this reaction system. The second-order rate constants, \( k_2^A \), obtained for this system are in Table (3.7) together with the corresponding polar substituent constants, \( \sigma^* \) and the steric substituent constant, \( E_s^* \). Correlation analysis of the log \( k_2^A \) values, with the relevant \( \sigma^* \) and \( E_s^* \) values, gave results which gave a Taft equation as follows:

\[
\log k_2^A = -0.520 + 0.828 \sigma^* + 0.198 E_s^* \tag{3.34}
\]

The correlation coefficient, \( R \), was 0.974 with a standard error, \( S \), of 0.116. This indicates that polarity dominates in this reaction scheme and that steric effects are of relatively little importance.

When the above treatment was applied after allowing for any spontaneous esterification reactions, values of which are given in Table (3.8), the Taft equation became

\[
\log k_2^A = -0.525 + 0.770 \sigma^* + 0.197 E_s^* \tag{3.35}
\]

With \( R = 0.968 \) and \( S = 0.121 \)

The slightly poorer correlation may suggest that the presence of TiTE inhibits the spontaneous esterification reaction and renders the above correction unnecessary. This observation agrees with other evidence already obtained in this study. The spontaneous esterification reaction depends on the \( K_a \) value of the acid. It has already been established that TiTE is capable of acetate
ion formation when in the presence of acetic acid (see 3.1.1). If the TiTE removes protons in the presence of substituted acetic acids, this will then hinder the spontaneous esterification reaction.

These observations agree with those of Habib and Malek who observed that the kinetic treatment of the esterification of benzoic acids with glycols in the presence of titanium alkoxides was in best agreement when the spontaneous esterification rates were neglected. However in high-temperature esterification of phthalic acid monoesters with low concentrations of titanium alkoxides, the parallel and essentially uninhibited spontaneous esterification is very evident, indeed dominant initially, becoming less significant at higher conversions owing to its higher order with respect to carboxylic acid.
(3.2) Titanium Tetra-n-Butoxide

(3.2.1) Introduction

The acetic acid, butan-1-ol, and titanium tetra-n-butoxide system was the first studied in this work. Initial experiments involving varying the acetic acid and the titanium tetra-n-butoxide concentration at 110°C were undertaken once the experimental and analytical procedure discussed in Chapter 2 had been developed. The form of the extent of reaction-versus-time plots obtained for these reactions was such that a straightforward kinetic treatment was not possible, see Fig. (3.21) for example. Initial rates were determined, \( t = 0 \) being taken after 5 min. which was the time taken for the contents of the reaction tube to reach 110°C. A double front surface mirror was used to draw a normal and then a tangent at \( t = 0 \) to the reaction-versus-time curve, the gradient of which gave the initial rate.

The apparent order, \( n_A \), of a particular reaction was determined by drawing normals and tangents at various points along the reaction-versus-time curve in a similar manner. The gradient of the double log plot of rate versus potassium methoxide titre gave the apparent order of reaction \( n_A \), see Fig. (3.22). Owing to the scatter of points on the graph, the value of \( n_A \) was only very approximate. The results obtained from various initial acetic acid and titanium tetra-n-butoxide concentrations are given in Table (3.13).

The order of reaction was also determined by using the initial rate values obtained after the variations of titanium tetra-n-butoxide and acetic acid assembled in Table (3.13).

All rates quoted are the arithmetic means of at least four independent determinations because of the poor reproducibility of results for this system. The given error limits are the maximum deviations found from the arithmetic means quoted.
Fig. (3.21) Reaction versus time plot for acetic acid (0.10M) with Ti(0Bu)$_4$ (0.02M) in butanol at 110°C.
Fig. (3.22) Double log plot of log Rate versus log potassium methoxide for acetic acid (0.10M) with Ti(OBu)_4 (0.02M) in butan-1-ol at 710°C in order to determine the apparent order of reaction n_A.
### Table 3.13

**Esterification of Acetic Acid with Butan-1-ol in the Presence of Titanium Tetra-n-Butoxide at 110°C**

<table>
<thead>
<tr>
<th>Acetic Acid M</th>
<th>Ti(OBu)$_4$ M</th>
<th>Water (added) M</th>
<th>50% Reaction Time in mins. (ave)</th>
<th>Order $n_A$</th>
<th>Rate at $t = 0 \times 10^4$ mol 1$^{-1}$ min$^{-1}$</th>
<th>Rate at $t = 0^\infty \times 10^4$ mol 1$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.005</td>
<td>-</td>
<td>174</td>
<td>2.22</td>
<td>$6.2 \pm 0.19$</td>
<td>$6.35 \pm 0.13$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.010</td>
<td>-</td>
<td>148</td>
<td>2.56</td>
<td>$8.7 \pm 0.17$</td>
<td>$8.18 \pm 0.43$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.015</td>
<td>-</td>
<td>127</td>
<td>2.88</td>
<td>$10.5 \pm 0.82$</td>
<td>$10.7 \pm 0.80$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>-</td>
<td>122</td>
<td>2.82</td>
<td>$11.8 \pm 0.18$</td>
<td>$13.3 \pm 0.13$</td>
</tr>
<tr>
<td>0.050</td>
<td>0.020</td>
<td>-</td>
<td>58</td>
<td>2.06</td>
<td>$8.0 \pm 0.43$</td>
<td>$8.92 \pm 0.50$</td>
</tr>
<tr>
<td>0.075</td>
<td>0.020</td>
<td>-</td>
<td>103</td>
<td>2.46</td>
<td>$10.6 \pm 2.7$</td>
<td>$12.5 \pm 1.10$</td>
</tr>
<tr>
<td>0.150</td>
<td>0.020</td>
<td>-</td>
<td>165</td>
<td>3.13</td>
<td>$14.1 \pm 2.5$</td>
<td>$15.1 \pm 0.39$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>$7.0 \pm 0.06$</td>
<td>$9.1 \pm 0.11$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>$9.0 \pm 0.10$</td>
<td>$9.6 \pm 0.30$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.063</td>
<td>-</td>
<td>-</td>
<td>$3.8 \pm 0.08$</td>
<td>$4.09 \pm 0.32$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.078</td>
<td>-</td>
<td>-</td>
<td>$3.3 \pm 0.01$</td>
<td>$4.20 \pm 0.21$</td>
</tr>
</tbody>
</table>

* Apparent order of reaction with respect to acetic acid as determined by a double log plot over the course of the given experiment.

* Rate at $t = 0$ determined from a second- or third-order plot.
(3.2.2) Discussion of the Kinetics of the Acetic Acid, Butan-1-ol and Ti(OBu)₄ System

The Form of the Reaction-Versus-Time Curves

The form of the reaction-versus-time curves observed for the titanium tetra-n-butoxide, acetic acid, butan-1-ol system suggested that attempted fitting of the data to second- or third-order equations might lead to more meaningful results than those obtained from the initial-rate method, see Fig. (3.23). This was done, and where the data approximated closely to a satisfactory second- or third-order rectilinear plot the value of the rate at \( t = 0 \) was determined from the gradient of a tangent to the plot at the origin. These results are given in Table (3.13). The gradient of the tangent had to be taken as the rate and not the gradient of the best straight line from the plot, because any deviations from simple kinetic behaviour which occur as the reaction proceeds would lead to an erroneous value of the initial rate.

(3.2.3) The Order of Reaction, \( n_A \), During the Course of a Particular Reaction

The values of the order, \( n_A \), with respect to acetic acid are greater than the expected value of one, see Table (3.13). This is consistent with the catalyst changing its reactivity with reaction time. This appears to be due to the effect of water liberated in the esterification; this water reacts with the titanium tetra-n-butoxide to produce species containing Ti-O-Ti linkages.

(3.2.4) The Effect of Water on the Ti(OBu)₄ - Acetic Acid - Butan-1-ol System

Results obtained for the addition of water to the titanium tetra-n-butoxide, butan-1-ol and acetic acid system at 110°C show the reaction to be extremely sensitive to the presence of water, see Table (3.13). The reaction-versus-time curve, however is still of the same form as that for a reaction where water had not been added, see Fig. (3.24).
Fig. (3.23) Second order plot for acetic acid (0.10M) with Ti(0Bu)$_4$ (0.02M) in butan-1-ol at 110°C.
Reaction versus time plot for acetic acid (0.10 M) Ti(OBu)₄ (0.02 M) with water (0.06 M) in butan-1-ol at 110°C.
Although Ti(OBu)$_4$ is sensitive to water it is not totally inactivated by it. A reaction was carried out in sealed glass tubes at 110°C. The reaction was shown to go to completion after about 1600 min. This showed that the reaction was not effectively reversible under these conditions and also that each molecule of water liberated did not completely inactivate one molecule of catalyst.

(3.2.5) The Order of Reaction, $n$, with Respect to Various Initial Ti(OBu)$_4$ and Acetic Acid Concentrations

The order of reaction, $n$, with respect to Ti(OBu)$_4$ concentration was found to be fractional, $n = 0.501$, see Fig. (3.25). This observation is consistent with a proportional reduction of catalytic activity with increase in Ti(OBu)$_4$ concentration. This may be due to oligomerisation of the Ti(OBu)$_4$ in butan-1-ol. Evidence of oligomerisation of Ti(OBu)$_4$ in ethanol was given in section (2.4). Oligomerisation of Ti(OBu)$_4$ would reduce the number of catalytically active sites as compared to the monomer. This can be compared to the results obtained for the TiTE system where there is evidence of some dimerisation; here the order of reaction with respect to TiTE concentration was found to be almost unity.

The order of reaction, $n$, with respect to acetic acid concentration was also found to be fractional, $n = 0.51$, see Fig. (3.26). This may be due to complex formation between Ti(OBu)$_4$ and acetic acid. Infra-red spectroscopic study of the system done in a manner similar to that for TiTE, see section (3.1.1), showed the formation of acetate ion when Ti(OBu)$_4$ was added to acetic acid in butan-1-ol.

These fractional values of $n$ agree with results from a study by Habib and Malek of esterification of carboxylic acids with glycols at higher temperatures using titanium-butoxide.

(3.2.6) The Activation Energy of the Acetic Acid, Butan-1-ol and and Ti(OBu)$_4$ System

Initial rates at $t = 0$ for a standard reaction mixture were also determined at 5°C intervals over the range 100-120°C, giving an activation energy of
Fig. (3.25) Double log plot of log Rate at t = 0 versus log Ti(OBu)$_4$ with acetic acid (0.10M) in butan-1-ol at 110°C to determine the order of reaction, $n$, with respect to Ti(OBu)$_4$. 
Double log plot of log Rate at $t = 0$ versus log acetic acid with Ti(ORu)$_4$ (0.02 M) in butan-1-ol at 110°C to determine the order of reaction, $n$, with respect to acetic acid.
18.4 ± 0.1 k cal mol⁻¹, see Table (3.14) and Fig. (3.27). The error limits quoted are determined by least squares analysis.

**TABLE (3.14)**

Esterification of Acetic Acid with Butan-1-ol in the Presence of Titanium Tetra-n-Butoxide at Several Temperatures

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Rate at t = 0, mol⁻¹ min⁻¹ x 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>7.16 ± 0.41</td>
</tr>
<tr>
<td>105.0</td>
<td>8.54 ± 0.62</td>
</tr>
<tr>
<td>110.0</td>
<td>11.8 ± 0.18</td>
</tr>
<tr>
<td>115.0</td>
<td>19.1 ± 1.73</td>
</tr>
<tr>
<td>120.0</td>
<td>23.7 ± 2.01</td>
</tr>
</tbody>
</table>
Fig. (3.27) Arrhenius plot for $\text{Ti(OBu)}_4(0.02\text{M})$ and acetic acid (0.10M) in butan-1-ol.
(3.3) Other Titanium Alkoxides

(3.3.1) Titanium Tetramethoxide

This white powder proved to be insoluble in butan-1-ol. It was therefore impossible to study this compound as a catalyst in esterification reactions.

(3.3.2) Titanium Tetraethoxide

This liquid was rapidly hydrolysed when it came into contact with moist air. Because of this only one reaction of this material was studied. This was for acetic acid (0.100 M) and titanium tetraethoxide (0.020 M) in butan-1-ol at 110°C. The form of the reaction-versus-time curve produced in this reaction was very similar to that for titanium tetra-n-butoxide, see Fig. (3.2a). The rate at \( t = 0 \) was \( 9.8 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1} \), cf. \( 1.18 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \) for titanium tetra-n-butoxide under comparable conditions. This suggests that a rapid exchange of the ethoxide ligands with butan-1-ol occurs to produce titanium tetra-n-butoxide. Titanium alkoxides are known to react with higher alcohols in such a manner.

(3.3.3) Titanium Tetraisopropoxide

This compound was also readily hydrolysed in the presence of moist air. A series of reactions was undertaken for acetic acid (0.10 M) and titanium tetraisopropoxide (0.020 M) in butan-1-ol at 110°C. The forms of the reaction-versus-time curves were again very similar to those for titanium tetra-n-butoxide. The rate at \( t = 0 \) was \( 1.30 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \), cf. \( 1.18 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \) for titanium tetra-n-butoxide under comparable conditions. The explanation for these results is as for the titanium tetraethoxide system

(3.3.4) Di-Isopropoxytitanium Bis-Acetylacetonate

![Diagram](image-url)
Fig. (3.28) Reaction versus time plot for acetic acid (0.10M) with titanium tetraethoxide (0.02M) in butan-1-ol at 110°C.  

of Ti(OBu)₄.
This alkoxide was briefly studied because its chelate bonds suggested a similarity to TiTE. Ti Acac is hydrolysed only slowly in water at room temperature. Experimental results for reactions with this compound as catalyst are in Table (3.15). The forms of the reaction-versus-time curves are similar to those for titanium tetra-n-butoxide but the resemblance is not as close as for titanium tetraethoxide and titanium tetraisopropoxide, see Fig. (3.30). The characteristic red colour of the catalyst was removed after a very short time when it was heated to 110°C in the reaction medium. An experiment in which Ti Acac had been refluxed in butan-1-ol for two hours before addition of acetic acid showed a reaction-versus-time curve closer to that for the titanium tetra-n-butoxide system, see Fig. (3.30).

The form of the reaction-versus-time curve and the above observations suggest that the two isopropoxy ligands in Ti Acac are rapidly converted into butoxy ligands which are initially protected by acetylacetonate ligands which inhibit hydrolysis of the catalyst by their bulky nature, thus preventing the formation of Ti-O-Ti linkages. Once these acetylacetonate ligands are removed the catalyst reacts in the manner of titanium tetra-n-butoxide.
Fig. (3.30) Reaction versus time plot for acetic acid (0.10M) in butan-1-ol at 110°C with various titanium alkoxides (0.02M).

- TiTE
- Ti(OBu)₄, Ti(0Pr)₄, or Ti(OEt)₄
- TiAcac
- TiAcac refluxed in butan-1-ol for 2 hours
TABLE (3.15)

Esterification of Acetic Acid with Butan-1-ol in the Presence of Ti Acac at 110°C

<table>
<thead>
<tr>
<th>Acetic Acid M</th>
<th>Ti Acac, M</th>
<th>Water, M added</th>
<th>Rate at $t = 0 \times 10^4$ mol l$^{-1}$ min.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.020</td>
<td>0.00</td>
<td>7.52</td>
</tr>
<tr>
<td>0.075</td>
<td>0.020</td>
<td>0.00</td>
<td>9.33</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.00</td>
<td>10.10</td>
</tr>
<tr>
<td>0.150</td>
<td>0.020</td>
<td>0.00</td>
<td>13.0</td>
</tr>
<tr>
<td>0.100</td>
<td>0.005</td>
<td>0.00</td>
<td>5.9</td>
</tr>
<tr>
<td>0.100</td>
<td>0.010</td>
<td>0.00</td>
<td>7.57</td>
</tr>
<tr>
<td>0.100</td>
<td>0.015</td>
<td>0.00</td>
<td>8.84</td>
</tr>
<tr>
<td>0.100</td>
<td>0.030</td>
<td>0.00</td>
<td>12.7</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.020</td>
<td>9.4</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.039</td>
<td>7.8</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020</td>
<td>0.100</td>
<td>6.4</td>
</tr>
<tr>
<td>0.100</td>
<td>0.020$^E$</td>
<td>0.000</td>
<td>10.5</td>
</tr>
</tbody>
</table>

$^E$ Ti Acac refluxed in Butan-1-ol for two hours before reaction
Summary and Conclusion

(4.1) The initial system chosen for study was titanium tetra-n-butoxide, acetic acid, and butan-1-ol. Initial rates, orders of reaction, activation energies have been determined. The complex nature of kinetics, due to the instability of titanium tetra-n-butoxide in the presence of water generated during esterification, made further study of the system impractical in the time available.

(4.2) The kinetics of the reaction of some other simple titanium alkoxides have been briefly studied but these also prove to be unsuitable catalysts, again because of their instability to water.

(4.3) Two titanium alkoxides containing chelating ligands were examined, because of their known resistance to hydrolysis. Di-isopropoxy titanium bis-acetylacetonate gave kinetics similar to those of the simple titanium alkoxides and was therefore discarded after a brief study. Bis-(triethanolamine) titanium di-isopropoxide (TITE) however gave a satisfactory first order plot up to 60 - 70 % reaction for acetic acid in butan-1-ol showing it to be more resistant to hydrolysis than the simple titanium alkoxides. A more detailed kinetic and mechanistic study of this catalyst was therefore undertaken.

(4.4) First-order rate constants and apparent second order rate constants for the reactions of TITE and acetic acid in butan-1-ol have been determined at temperatures between 80°C and 120°C. No significant change of kinetic behaviour was observed throughout this temperature range. The activation energy of this reaction was found to be 16.3 ± 0.3 kcal mole. A detailed study of the system at 110°C has been made.

(4.5) A mechanism has been proposed to explain the kinetics of the above reactions.

(4.6) The effect of TITE addition in raising the pH of acetic acid in butan-1-ol solutions has been studied. The observed pH values at zero potassium methoxide addition, half neutralisation and at the
end-point have been compared with those determined from available physical data for acetic acid, and found to differ considerably in each case.

(4.7) The effect of adding various quantities of potassium acetate and triethanolamine to the above reaction system has been studied. Triethanolamine has little effect on the system, but potassium acetate addition produced an increase in $k_A$ values. This has been shown not to be a salt effect. A mathematical treatment of possible equilibrium and rate processes occurring in the system has been undertaken. The result of this agreed closely with the experimental results.

(4.8) A Hammett treatment of the esterification of some meta- and para-substituted benzoic acids with butan-1-ol in the presence of TITE as catalyst has been done to discover more about the esterification mechanism. The Hammett plot shows satisfactory linear relationship between $\log k_A$ and the substituent constants, $\sigma$, with a reaction constant equal to $0.89 \pm 0.02$, compared to a value of $\rho = 0.57$ for acid catalysed esterification of substituted benzoic acids in methanol at 60°C. The TITE system shows that ease of esterification increases with acid strength. The result for $p$-methoxybenzoic acid—an anomaly in the Hammett treatment—is discussed.

(4.9) The esterification of some ortho-substituted benzoic acids with butan-1-ol in the presence of TITE as catalyst has been studied to show the magnitude of steric effects compared to polar effects of substituents. Steric hindrance is an important factor in the esterification of ortho-substituted benzoic acids.

(4.10) The precipitate formed between 3, 5-dinitrobenzoic acid and TITE in butan-1-ol has been analysed. The results from this have been used as a basis for a proposed structure of a reaction intermediate in the esterification reaction. Two possible structures are given.

(4.11) A Taft treatment of the kinetic results from the esterification of some substituted acetic acids with butan-1-ol in the presence of TITE
catalyst has been carried out, polarity dominates in this reaction scheme and steric affects are of less importance. The Taft treatment has also be carried out after allowing for any spontaneous esterification reactions. The results show that TITE may inhibit the spontaneous esterification reaction.
The Arrhenius parameters, $E$ and $\log A$, were calculated by using the Arrhenius equation

$$k = A e^{-E/RT}$$

$$\log k = \log A - \frac{E}{2.303 RT}$$

The related parameters of transition state theory, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are given by the expressions

$$\Delta H^\ddagger = E - RT$$

and

$$\Delta S^\ddagger = 2.303 R ( \log A - \log k_B T / h ) - R$$

where $k_B$ is Boltzmann's constant, $h$ is Planck's constant, and $R$ is the gas constant.
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