International Journal of Advanced Research and Development
ISSN: 2455-4030
Impact Factor: RJIF 5.24
www.advancedjournal.com
Volume 3; Issue 1; January 2018; Page No. 293-295

A study on esterification: A case study of esterification of trifluoroacetic acid with phenyldiazo

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Abstract
Trifluoroacetic acid in biological materials has been quantitatively determined by gas chromatography. Benzyl trifluoroacetate has been prepared by the reaction of the acid with phenyldiazomethane, and has been successfully analyzed by gas chromatography without any interference from other peaks. The procedure has been used to determined trifluoroacetic acid in microsomal suspension incubated with halothane, a gaseous anaesthetic.

Keywords: trifluoroacetic, phenyldiazo, esterification

Introduction

Esters are most commonly prepared by the reaction of a carboxylic acid and an alcohol with the elimination of water. Esters are also formed by a number of other reactions utilizing acid anhydrides, acid chlorides, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes, ketones, alcohols, and esters.

In making acetate esters, the primary alcohols are esterified most rapidly and completely, ie, methanol gives the highest yield and the most rapid reaction. Ethyl, n-propyl, and n-butyl alcohols react with about equal velocities and conversions. Under the same conditions, the secondary alcohols react much more slowly and afford lower conversions to ester products; however, wide variations are observed among the different members of this series. The tertiary alcohols react slowly, and the conversions are generally low (1−10% conversion at equilibrium). With isobutyl alcohol at 155°C, acids containing a straight-chain (acetic, propionic, and butyric) and phenylacetic and β-phenylpropionic acids are esterified readily. Formic acid has the highest initial rate of reaction.

The introduction of a branched chain in the acid decreases the rate of esterification, and two branches cause a still greater retarding effect. However, the conversions to ester products from these substituted acids is higher than for the normal straight-chain acids. Similarly, aromatic acids, benzoic and p-toluic, react slowly but have high equilibrium conversions. The introduction of a nitrile group on an aliphatic acid has a pronounced inhibiting effect on the rate of esterification. With the chloroacetic acids, the velocity decreases with increased chlorination. Double bonds also have a retarding influence on the rate of esterification. Tests on substituted acrylic acids have shown that α,β-unsaturated acids are esterified much less easily than the saturated analogues. A triple bond in the α,β position has about the same effect as a double bond.

Because the esterification of an alcohol and an organic acid involves a reversible equilibrium, these reactions usually do not go to completion. Conversions approaching 100% can often be achieved by removing one of the products formed, either the ester or the water, provided the esterification reaction is equilibrium limited and not rate limited. A variety of distillation methods can be applied to afford ester and water product removal from the esterification reaction.

Esters of high volatility, such as methyl formate, methyl acetate, and ethyl formate, have lower boiling points than those of the corresponding alcohols, and therefore can be readily removed from the reaction mixture by distillation.

Esters of medium volatility are capable of removing the water formed by distillation. Examples are propyl, butyl, and amyl formates, ethyl, propyl, butyl, and amyl acetates, and the methyl and ethyl esters of propionic, butyric, and valeric acids. In some cases, ternary azeotropic mixtures of alcohol, ester, and water are formed. This group is capable of further subdivision: with ethyl acetate, all of the ester is removed as a vapor mixture with alcohol and part of the water, while the balance of the water accumulates in the system. With butyl acetate, on the other hand, all of the water formed is removed overhead with part of the ester and alcohol, and the balance of the ester accumulates as a high boiler in the system.

Esters of low volatility are accesible via several types of esterification. In the case of esters of butyl and amyl alcohols, water is removed as a binary azeotropic mixture with the alcohol. To produce esters of the lower alcohols (methyl, ethyl, propyl), it may be necessary to add a hydrocarbon such as benzene or toluene to increase the amount of distilled water. With high boiling alcohols, ie, benzyl, furfuryl, and β-phenylethyl, an accessory azeotroping liquid is useful to eliminate the water by distillation.

Acidolysis requires the sue of an elevated temperature, the use of an acid catalyst (7), or both. Like alcoholysis, the reaction is reversible and requires the use of an excess of the replacing acid or removal of one of the products from the reaction if a high degree of replacement of the acid radical of an ester by another acid is to be obtained. This can be accomplished by distilling one of the products from the reaction mixture during the acidolysis

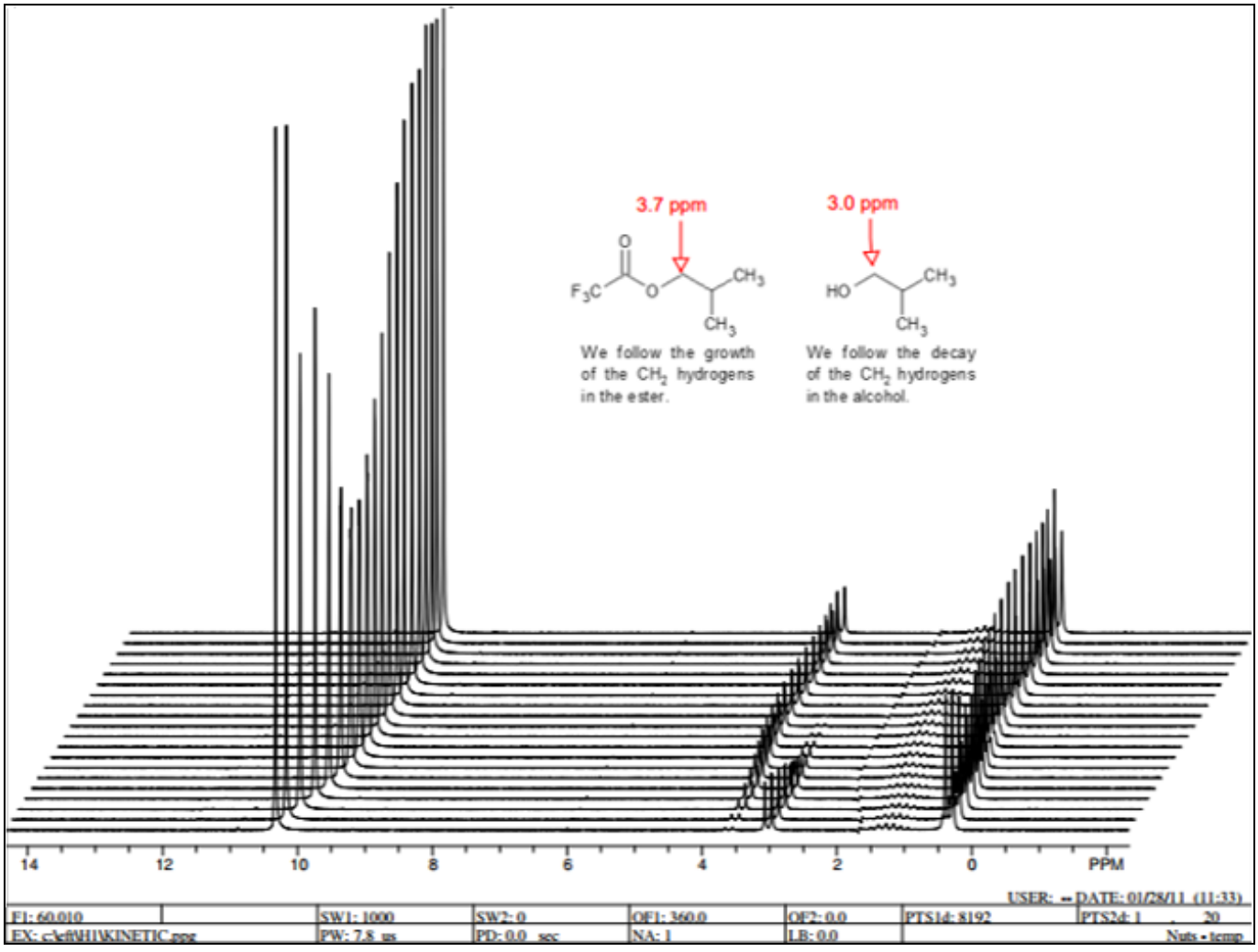
Methodology

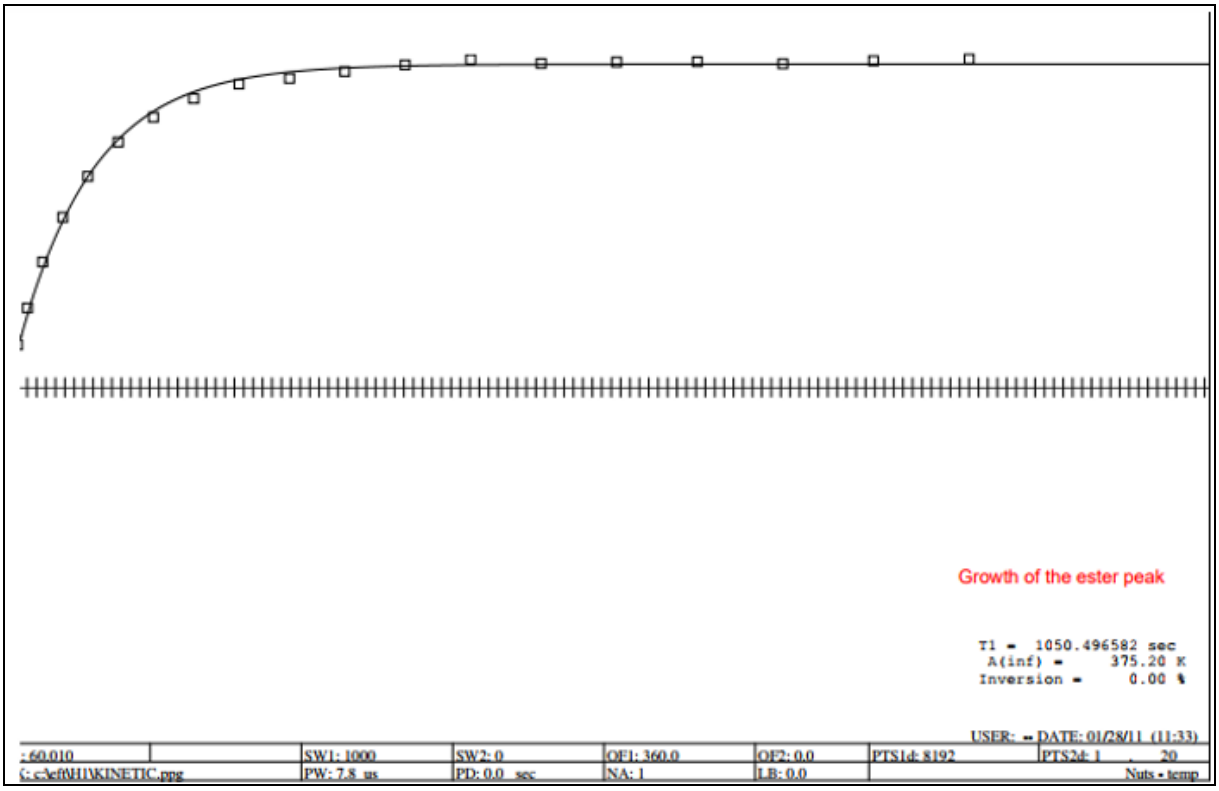
Synthetic peptide or protein samples are mostly unpurified with trifluoroacetic acid (TFA) used during the synthesis

procedure, which strongly interferes with structure determination by infrared (IR) spectroscopy. The aim of this work was to propose a simple strategy to remove TFA contribution from attenuated total reflection (ATR)–IR spectra of the hexahistidine peptide (His6) in aqueous solution to study the conformation of this synthetic peptide without previous purification. Such a strategy is based on the subtraction mode widely employed to remove water contribution, and it is tested with TFA unpurified histidine as a model system. The subtraction is based on eliminating the strong TFA bands at 1147 and 1200 cm^{-1} by applying a scaling factor (as in buffer correction). The proposed modes represent excellent strategies that do not modify spectral features, and they provide reliable routines to obtain the synthetic peptide spectrum without TFA contribution. The conformational information from the corrected spectra at different pH values is deduced from semiempirical calculated IR spectra of different His6 conformers. The spectral features and the band positions of the corrected spectrum suggest that the peptide molecules mainly adopt an intermolecular β-sheet structure.

Results

We obtain the kinetics data by taking a series of 1H NMR scans over time, as the reaction progresses. We can follow a product peak as it grows in, or a reactant peak as it decays away. Typical data for methanol, ethanol, isopropy alcohol and isobutyl alcohol are shown on the attached pages. If we zoom in on the peak of interest, the NUTS software will calculate a "T1" value that represents the reciprocal of the rate constant.





Conclusion

Esterification can occur only when the concentrations of the acid and alcohol are in excess of equilibrium values; otherwise, hydrolysis must occur. The equations governing the rate of the reaction and the variation of the rate constant (as a function of such variables as temperature, catalyst strength, and proportion of reactants) describe the kinetics of the liquid-phase reaction. The usual distillation laws must be modified, since most esterifications are somewhat exothermic and reaction is occurring on each plate. Since these kinetic considerations are superimposed on distillation operations, each plate must be treated separately by successive calculations after the extent of conversion has been determined.

Esterification is generally carried out by refluxing the reaction mixture until the carboxylic acid has reacted with the alcohol and the water has been split off. The water or the ester is removed from the equilibrium by distillation. The choice of the esterification process to obtain a maximum yield is dependent on many factors, ie, no single process has universal applicability. Although extensive preparative techniques have been reviewed elsewhere.

In general, the same catalysts are effective as in alcoholysis. Usually the reaction is slower than alcoholysis of the same esters. Without a catalyst, a reaction time of several hat >250±C is required to bring two typical esters to equilibrium. Catalysts are almost essential to bring reaction rates into a practical range so that the use of destructive temperatures can be avoided. Tin compounds, especially stannous hydroxide, have been mentioned frequently as catalysts and do not produce much decomposition or discoloration of the esters. More effective at lower temperatures are the acid catalysts, such as sulfuric acid and sulfonic acids, and especially the alkaline catalysts such as sodium alkoxides. With an alkaline catalyst, ester−ester interchange can be carried out at temperatures as low as 0°C.

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