Asian Journal of Chemistry Vol. 1, No. 1 (1989), 70–74

A Study of Reaction of n-Butyl Alcohol and n-Butyric Acid in Presence of Thionyl Chloride

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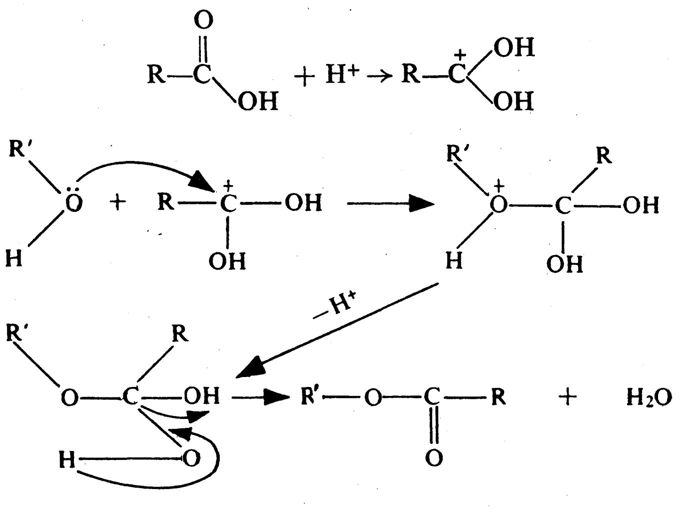
Esterification reaction between n-butyl alcohol and n-butyric acid in presence of thionyl chloride has been studied. The reaction can be described as an organo-inorganic reaction giving 20% and 30% ester (0.2 mol acid : 0.2 mole and 0.4 mole thionyl chloride), at zero hr and at ambient temperature. The reaction has been so described as even though organic reactions are slow (covalent bonding), formation of ester is instantaneous as inorganic reaction e.g. precipitation of silver chloride from silver nitrate solution and chloride ions (electrolytes).

INTRODUCTION

Preliminary observations are made on the mechanism of the effect of thionyl chloride on the ester forming reactions between n-butyl alcohol and n-butyric acid at ambient temperature in presence of non-polar solvent.

The reaction of alcohol and organic acid is reversible. It is customary to heat the reaction mixture for speeding up the esterification. It has long been known that the process may be hastened by the addition of a strong acid such as sulphuric acid or hydrochloric acid[1]. But the addition of the catalyst does not alter the equilibrium. Acceleration of esterification is due to the hydrogen ions forming oxonium ions with the acid to be esterified[2]. Hydrogen ions similarly influence the reverse reactions of esterification.



Use of acid chlorides has been made in esterification reactions 3–7. The reaction results in the formation of hydrogen chloride.

Thionyl chloride at high temperature has been used for esterification of phenol and salicylic acid.[8] Thionyl chloride was used as esterification catalyst (0.5 mol.) at ambient temperature. Method of esterification by using thionyl chloride at ambient temperature was extended by Prabhudesai[5] of this laboratory to prepare fatty, cholesteryl and other esters.

For esterification and interesterification of oleic acid and palm oil, Prabhudesai[6] used high excess of an alcohol that can absorb large quantities of HCl gas and thionyl chloride (0.7 mol.) with respect to acid and while preparing stearoyl and palmitoyl glycol esters[7] a non-polar solvent and a high excess of thionyl chloride had been used and he reported 96% esterification by chromatography.

The conditions in the above two methods are totally different. The second reaction had been carried out with molar quantities of the required alcohol and a non-polar solvent.

The purpose of this communication is therefore to make preliminary observations on the mechanism of thionyl chloride catalysed esterification reaction in presence of a non-polar solvent.

EXPERIMENTAL

Materials and Methods

n-Butyric acid, n-butyl alcohol, solvent ether, petroleum ether (40°–60°), butyl chloride, butyryl chloride, thionyl chloride and phosphorous trichloride (L.R. grade) were used. Petroleum ether was dehydrated over anhydrous sodium sulphate and used.

General method of preparation of ester was to take petroleum ether in a flask fitted with a condenser and n-butyric acid (17.6 g) and **n-butyl** alcohol (14.8 g) were added to it. Thionyl chloride (0.2 mole) was poured down cautiously through the condenser with shaking. The condenser was then washed with petroleum ether to make the total volume of ether (50 ml). Whole assembly had been kept in cold water (25°). After predetermined time (0 hr, 6 hr, 12 hr, 24 hr) the reaction mixture was poured down in water and immediately extracted with ether. The extract was washed completely with saturated sodium bicarbonate and then with water. It was dried over anhydrous sodium sulphate and ether was distilled out. Ester from residue was collected at 160–65° and weighed.

All the reactions were carried out at ambient temperature (25°–28°) and using the reactants in 0.2 : 0.2 molar proportion.

RESULTS AND DISCUSSION

At the ambient temperature the ester formation is slow, as will be seen from the following data[8]. Geraniol and linalool one mole each were mixed with acetic acid (6 moles) and esterification was studied at ambient temperature.

TABLE 1

TIME AND ESTER %

	24 hrs.	10 days	24 days	5 months
Geraniol	5.5	29.2	45.0	85.6
Linalool	0.4	0.6	1.1	3.9

n-Butyl alcohol is also a primary alcohol so by analogy we can expect about the same % formation of ester namely five per cent maximum after 24 hr. So measurable ester formation cannot be expected in case of n-butyl alcohol and n-butyric acid within a short time at ambient temperature.

$$C_4H_9OH + C_3H_7COOH \rightarrow C_4H_9OOCC_3H_7 + H_2O$$

Thionyl chloride and phosphorous trichloride catalyse the reaction and yields of ester are (A) with 0.2 mol thionyl chloride, 0 hr —20.8%, 6 hr 29.3%, 9 hr 34.8% and 12 hr 50.0% and (B) with 0.4 mole thionyl chloride, 0 hr —29.8%, 6 hr 32.1%, 9 hr 34.8% and 12 hr 57.2%; (C) with phosphorous trichloride 12.0% ester at 0 hr and about the same quantity of phosphoric acid derivative was obtained.

Thionyl chloride serves as a chlorinating agent for replacing hydroxyl group by chlorine group so also phosphorous trichloride and react at ambient temperature with n-butyl alcohol to give n-butyl chloride and with n-butyric acid, to produce n-butyryl chloride. With a view to find out the part played by these two chlorides in the ester formation, the reactions between: (1) n-butyl chloride and n-butyric acid, and (2) n-butyryl chloride and n-butyl alcohol were investigated. The first reaction did not give any ester whereas in the second reaction the yields were 0 hr, 1.5% and 6 hr 20.0%. The two-steps process involving the formation of butyryl chloride is the first instance and its subsequent reaction with butyl alcohol cannot explain initial high yield of ester at 0 hr (20 and 30% against 1.5% obtained in case of n-butyryl chloride and a butyl alcohol) in the reaction between n-butyl alcohol and n-butyric acid in presence of thionyl chloride and phosphorous trichloride.

The overall equations for the thionyl chloride catalysed reactions may be given as

I. (i) $C_4H_9OH + C_3H_7COOH \rightarrow C_4H_9O{\cdot}OC{\cdot}C_3H_7 + H_2O$

(ii) $H_2O + SOCl_2 \rightarrow 2\ HCl + SO_2$

II. $C_4H_9OH + C_3H_7COOH + SOCl_2 \rightarrow C_4H_9O{\cdot}OC{\cdot}C_3H_7 + SO_2 + HCl$

In case I water formed in esterification reaction is removed by thionyl chloride, itself having affinity for water producing HCl serving as a catalyst for esterification and esterification may further proceed as equilibrium in Equation I becomes unbalanced in favour of forward reaction as in case II.

During next 12 hr about 30% further esterification is observed. This is considered to be produced by the reaction between n-butyryl chloride and n-butyl alcohol. It may be mentioned that the analysis of the reaction mixture showed the presence of butyryl chloride, was: in (A) after 6 hr butyl chloride 10.0% and butyryl chloride 20.0%, and in (B) after 9 hr butyl chloride 15.0% and butyryl chloride 20.0%. Butyl chloride formed does not participate in the ester formation. Heating accelarates the esterification and on distilling out the ester about 80.0% yield of ester is obtained. In no case 96% ester could be obtained as reported[5].

The increase in the proportion of thionyl chloride enhances the initial yield of the ester but does not significantly influence the further esterification reaction. This is in accordance with the facts referred above that if extra quantity of thionyl chloride be considered, much of it has been utilised in enhancing the ester formation and decomposed. Due to dilution of the reactants the reactants having formed all the three products in the reaction, further significant increase cannot be obtained. The structure of thionyl chloride is pyramidal the S atoms using the sets of sp^3 hybrid orbitals, one of which holds the unshared pair of electrons. The S—O bonds are resonance hybrid of three canonical structures.

$$\overset{+}{S}-\overset{-}{O} \qquad S=O \qquad \overset{-}{S}\equiv\overset{+}{O}$$

The multiple bonding results from overlap of p orbitals of oxygen with empty d orbitals of sulphur. The bond order is about 2 as indicated by the bond distance which is 1.45 Å as compared to 1.7 Å expected for S—O single bond. As a result thionyl chloride can function as a weak Lewis base using lone pair of oxygen and as a weak Lewis acid using the vacant orbitals. Accordingly the intermediate steps of thionyl chloride catalysed reaction can be given by equations 2 and 3, $C_3H_7COSOCl$ is not stable and instantaneously reacts with alcohol to produce ester. Thionyl chloride abstracts OH from a butyric acid and H from a butyl alcohol and a molecule of water is eliminated. The interactions of thionyl chloride and H and OH equivalents to water molecule yield sulphur dioxide and hydrochloric acid. These interactions can be represented by eq. 2 and 3.

$$SOCl_2 + H^+ \rightarrow SOCl^+ + HCl \qquad (2)$$

$$SOCl^+ + OH^- \rightarrow SO_2 + HCl \qquad (3)$$

The initial instantaneous reaction may therefore be due to both the mechanisms I and II and HCl formed in the reaction. The reactions are being further studied to know exactly about the mechanism or mechanisms involved.

REFERENCES

1. A. I. Vogal, A Text Book of Practical Organic Chemistry, Longmans, London, p. 379 (1961).
2. M. Bremer and W. Huber, *Helv. Chim. Acta*, **36**, 1109 (1963).
3. E. Taschner and C. Waseilewski, *Annalen.*, **640**, 136 (1961).
4. B. T. R. Iyengar and H. Schlenck, *Lipids*, **4**, 28 (1969).
5. A. V. Prabhudesai, Ph.D. Thesis, University of Poona, p. 7 (1978).
6. W. F. Stoffel, F. Chu and E. H. Arhans, *Anal. Chem.*, **31**, 307 (1959).
7. F. Albert Cotton and C. I. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, New Delhi, p. 554 (1972).
8. Hans Meyer, Lehrbuchder Organisch Chemiken Methoden, Verlag von Julius Springer, Berlin, p. 612 (1912).

[*Received*: 15 March, 1988; *Accepted*: 12 October, 1988]