

Conductimetric and Potentiometric Investigation of Effects of Solvents and Titrant on Formation of Homoconjugates

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Received 12.02.2001

Trichloro-, tribromo- and trifluoro- acetic acids were both conductimetrically and potentiometrically titrated in acetonitrile and 2-propanol media. The titrations were carried out at 25°C under nitrogen atmosphere and titrants used were the solutions of triethyl, di-n-butyl and n-butyl amines prepared in the same solvents. Whether these acids gave a homoconjugation reaction during titration was investigated by the use of conductimetric and potentiometric titration curves. In acetonitrile media trichloro- and tribromo-acetic acids decomposed to give chloroform and carbon dioxide, and bromoform and carbon dioxide respectively. It was observed that the acid concentration and the type of titrant used had no effect upon the decomposition reaction. However, trifluoroacetic acid was seen to give a homoconjugation reaction when three titrants mentioned above were employed. When all three acids were conductimetrically titrated with three different titrants in 2-propanol medium, in order to elucidate the role of the medium upon the homoconjugation and decomposition reactions, it was observed that they gave stoichiometric end-points and the tendency to give homoconjugation decreased in this medium. The potentiometric titration results also support the conductimetric titration data. It was observed that the strength of the acid is important in the homoconjugation reaction.

Key Words: Non-aqueous media, conductimetric titration, potentiometric titration, trifluoroacetic acid, trichloroacetic acid, tribromoacetic acid, acetonitrile, 2-propanol.

Introduction

When an acid of intermediate strength is titrated conductimetrically with a base of intermediate strength in a solvent of low or relatively low dielectric constant that is a non-hydrogen bond donor (such as acetonitrile), homoconjugation reactions take place and homoconjugates are formed as follows:



where HA is an acid of intermediate strength and A⁻ is its conjugate base [1-9]. Homoconjugation accounts for the fact that in the conductimetric titration of acids of intermediate strength with aliphatic amines

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a maximum conductance is observed in the neighbourhood of 50% neutralisation [10-12]. In this study, trichloro-, tribromo-, and trifluoro-acetic acids were titrated conductimetrically and potentiometrically with triethylamine, n-butylamine and di-n-butylamine in both acetonitrile and 2-propanol. We carried out the present work in order to investigate the effects of structures and concentrations of acid titrated, solvent and titrant on the formation of homoconjugates.

Experimental

Apparatus

For the conductimetric titrations, an ORION Model 101 conductivity meter equipped with an Orion Cat. No. 99.01.01 conductivity cell (with a cell constant of 1.04 cm^{-1}) was used. All titrations were carried out in a specially designed cell described in Ref. 13. The cell was connected to a water-circulating thermostat.

For the potentiometric titrations, an Orion 720 model digital pH-ionmeter equipped with a combined glass electrode and a modified Ag-AgCl electrode was used. The Ag-AgCl electrode was modified by emptying its aqueous KCl solution and refilling it with a saturated solution of KCl in dry methanol.

Chemicals

Trichloroacetic acid and tribromoacetic acid were purchased from Fluka in 98% purity and trifluoroacetic acid was purchased from Merck in 99% purity. Three acids were used without further purification. Triethylamine (98%), n-butylamine (98%) and di-n-butylamine (99%) were purchased from BDH. Acetonitrile was purchased from Merck and purified as described previously [14]. 2-Propanol (Merck) was used after distillation over CaO.

Procedures

Conductimetric titrations were performed at 25°C; thermostating of the cell was used. The same conditions also applied to potentiometric titrations.

Solutions of triethylamine, n-butylamine and di-n-butylamine prepared in acetonitrile and in 2-propanol were standardised by the titration of standard perchloric acid solution. Then 0.050 M, 0.100 M and 0.150 M solutions of acids were titrated with 0.100 M triethylamine, 0.100 M n-butylamine and 0.100 M di-n-butylamine both in acetonitrile and in 2-propanol. All titrations were carried out under a nitrogen atmosphere.

Results and Discussion

This study was carried out to investigate whether trichloro-, tri-bromo- and trifluoro-acetic acids give homoconjugation reactions when they are titrated with triethylamine in acetonitrile medium. For this purpose, 0.100 M solutions of these three acids in acetonitrile were conductimetrically titrated with triethylamine solution prepared in acetonitrile. The conductimetric titration curves of trichloro- and trifluoro- acetic acids are given in Figures 1(b) and 2(b) respectively. As can be seen from the titration curve of trichloroacetic acid, the initial conductivity of this acid solution is very low, but it increases on the addition of triethylamine and then decreases very sharply before the stoichiometric end-point is reached. Following this decrease, there was no change in conductivity, even with excessive addition of the base. As a result of this,

there was no stoichiometric end-point for trichloroacetic acid. In the literature it was reported that there was a homoconjugation reaction in the titration of trichloroacetic acid under these conditions and it gave similar curves as those of trifluoroacetic acid given in Figure 2 [15]. However, our findings indicate that trichloroacetic acid decomposed under these conditions. In these types of titrations the conductivity first increases upon the addition of 0.1-0.2 mL titrant, then decreases gradually within 30-45 min and thereafter remains constant. Therefore, the further addition of titrant following an addition before waiting for the reaction to reach equilibrium results in the appearance of a false end-point. In the literature it was reported that trichloroacetic acid and some tertiary bases decompose to give chloroform and carbon dioxide in some solvents [6]. The fact that the curves obtained for tribromoacetic acid were similar to those obtained for trichloroacetic acid led us to conclude that tribromoacetic acid decomposed to give bromoform and carbon dioxide [16].

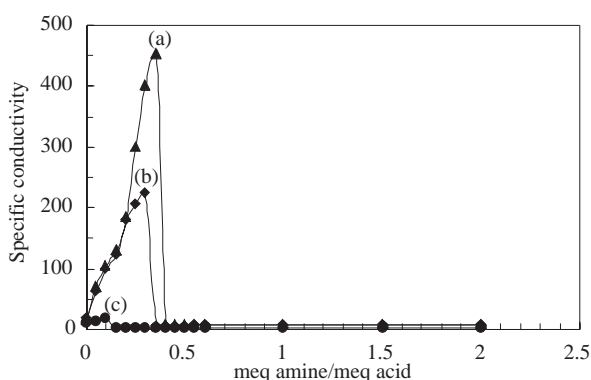


Figure 1. The conductimetric titration of trichloroacetic acid solutions with 0.100 M triethylamine in acetonitrile solvent: acid concentrations, (a) 0.150 M, (b) 0.100 M and (c) 0.0500 M.

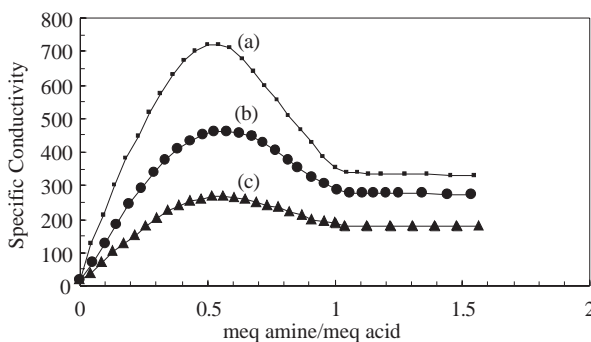


Figure 2. The conductimetric titration of trifluoroacetic acid solutions with 0.100 M triethylamine in acetonitrile solvent: acid concentrations, (a) 0.150 M, (b) 0.100 M, (c) 0.0500 M.

The conductimetric titration curves of trifluoroacetic acid given in Figure 2 show that it is possible to obtain stoichiometric titration curves for this acid. It is observed that conductivity increases upon the addition of triethylamine solution to trifluoroacetic acid solution up to the 50% neutralization point; then it decreases gradually and remains unchanged after the end-point. This implies that trifluoroacetic acid forms homoconjugates up to the 50% neutralization point under the conditions employed. This situation was reported for some compounds such as mono- and di-chloroacetic acid and the conductometric titration curves are similar to those obtained for trifluoroacetic acid [1].

0.050 M and 0.150 M solutions of these three acids were titrated with triethylamine in acetonitrile in order to investigate the effect of acid concentration on homoconjugation reactions, and the titration curves of trichloro- and trifluoro- acetic acids are given in Figure 1 (a, c) and Figure 2 (a, c). As seen from these curves both trichloro- and tribromo- acetic acids are decomposed at these concentrations and trifluoroacetic acid gives a homoconjugation reaction. It can be concluded that the concentration of the acid titrated does not have a significant effect upon homoconjugation and decomposition reactions.

The three acids were titrated with n-butyl- and di-n-butyl- amines instead of triethylamine in acetonitrile media in order to investigate the effect of the titrant used upon homoconjugation, and the titration curves for 0.100 M trichloroacetic acid are given in Figure 3. This figure also reveals that when primary or secondary amines are used as a titrant trichloroacetic acid undergoes decomposition. In addition, Figure 3 shows that decomposition in the case of n-butylamine takes place later. Provided that both titrations were carried out on the same time scale, this shows that n-butylamine decomposition is indeed slower. Similar results were obtained with tribromoacetic acid. Trifluoroacetic acid on the other hand was observed to give homoconjugation with the use of n-butyl- and di-n-butyl- amines as titrants and gave similar titration curves to those obtained with triethyl amine. In conclusion it can be stated that the use of a primary, secondary or tertiary amine as a titrant has no effect upon homoconjugation or decomposition reactions.

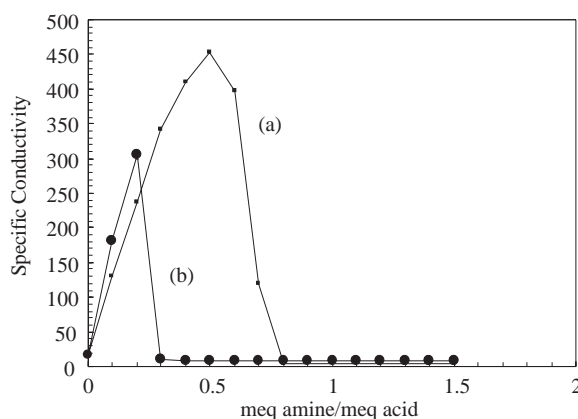


Figure 3. The conductimetric titration of 0.100 M trichloroacetic acid with (a) 0.100 M n-butylamine and (b) 0.100 M di-n-butylamine in acetonitrile solvent.

These three acids were also titrated in 2-propanol medium in order to elucidate the effect of the solvent upon the homoconjugation or decomposition reactions. 2-Propanol is a more polar solvent than acetonitrile, which can make hydrogen bonds. The titration curves obtained for trichloroacetic acid at three different concentrations with the use of triethylamine prepared in 2-propanol medium are given in Figure 4 as an example. It is seen from the curves that it is possible to obtain stoichiometric end-points for this acid. Tribromoacetic acid gave similar results.

The results obtained from the titration curves of the acids with n-butyl- and di-n-butyl- amines were similar. Figure 5 displays the titration curves of trifluoroacetic acid with three different titrants as an example. The titration curves of trichloro- and tribromo- acetic acids are similar to that of trifluoroacetic acid. The shape of the titration curves shows that the tendency to give a homoconjugation reaction in these three acids is decreased in 2-propanol and they can be titrated without being decomposed. This indicates that the solvent has a significant role in the decomposition of trichloro-, tribromo- and trifluoro- acetic acids. Thus, it shows that the choice of reaction media is of great importance.

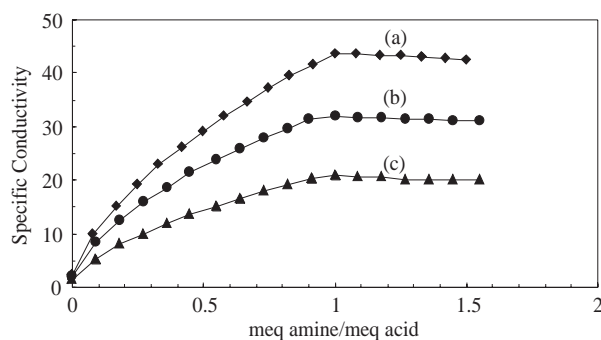


Figure 4. The conductimetric titration of trichloroacetic acid solutions with 0.100 M triethylamine in 2-propanol solvent: acid concentrations, (a) 0.150 M, (b) 0.100 M, (c) 0.0500 M.

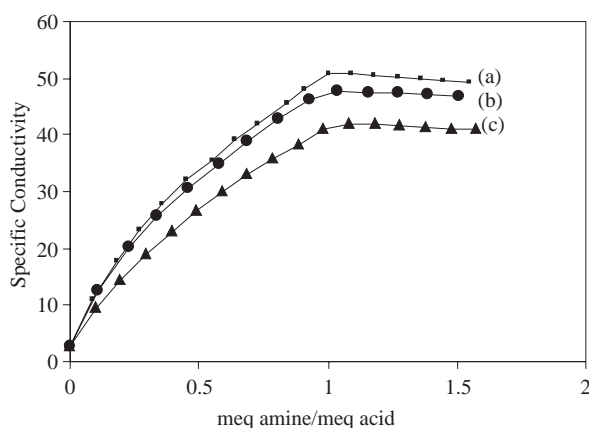


Figure 5. The conductimetric titration of 0.100 M trifluoroacetic acid solutions with (a) 0.100 M triethylamine, (b) 0.100 M n-butylamine and (c) 0.100 M di-n-butylamine in 2-propanol solvent.

In addition, the fact that only trifluoroacetic acid can be titrated in acetonitrile media without becoming decomposed reveals that the type of halogen atom in the acid structure has an effect equally important as that of the solvent in their titration without decomposition. This can be explained by the fact that chlorine and bromine atoms cause strains in the structure since they are larger than fluorine.

Furthermore all three carboxylic acids were potentiometrically titrated with three different amines in the same media in order to support the data obtained from the conductimetric titrations. The titrations of trichloro- and tribromo- acetic acids in acetonitrile media did not give characteristic S-type curves. Figure 6 is an example of the potentiometric titration curve of trichloroacetic acid. This figure shows that potential undergoes a sharp decrease initially upon the addition of amine to the medium and becomes constant before the end-point is reached. This indicates that these two acids decompose in this medium. Figure 7 gives the potentiometric titration curves of trifluoroacetic acid in acetonitrile medium. These curves enable the determination of the stoichiometric end-points. A careful examination of these curves shows that there was a large change in potential upon each addition of base before the end-point. This supports the fact that trifluoroacetic acid gives homoconjugation in this medium.

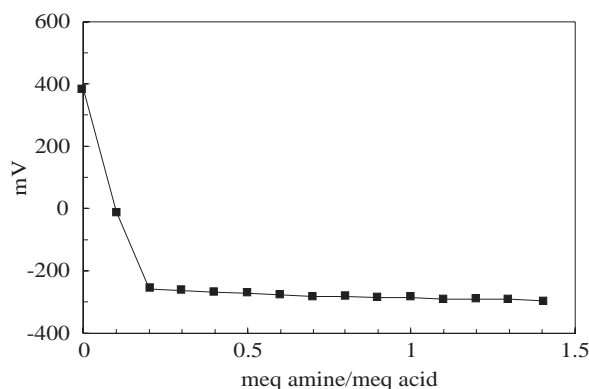


Figure 6. The potentiometric titration of 0.100 M trichloroacetic acid with 0.100 M triethylamine in acetonitrile.

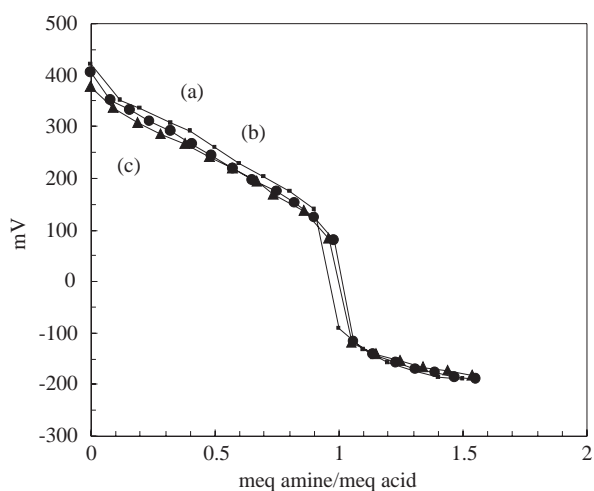


Figure 7. The potentiometric titration of trifluoroacetic acid with 0.100 M triethylamine in acetonitrile: acid concentrations, (a) 0.150 M, (b) 0.100 M and (c) 0.0500 M.

The fact that all three acids gave regular potentiometric titration curves with all three bases in 2-propanol medium reconfirms that the tendency of these compounds to give a homoconjugation reaction is lower in this medium. This can be explained by the fact that the acid is stabilized by the hydrogen bonds formed between the acid molecules and 2-propanol.

Conclusion

The conclusions drawn from both potentiometric and conductimetric titration data of trichloro-, trifluoro- and tribromo- acetic acids with triethyl, di-n-butyl and n-butyl amines are the following:

1. Repeated titrations of these three acids in acetonitrile medium showed that trichloro- and tribromo- acetic acids decompose to give chloroform and carbon dioxide, and bromoform and carbon dioxide, respectively. These are in good accordance with the literature [6]. Trifluoroacetic acid, on the other hand, gives homoconjugation in this medium.
2. It was observed that all three acids could be titrated in 2-propanol media to give stoichiometric end-points. This indicates that the solvent employed has an important role in the decomposition and the homoconjugation reactions of the acids used.

3. The investigation of conductimetric titration curves of these acids showed that the acidity of the acid, rather than the basicity of its conjugate base, plays a major role in the formation of homoconjugate ions, at least in acetonitrile solvent [1]. If the acid is strong enough, there is a maximum before the experimental end-point at about the half-neutralization point. The strongest one among these acids in water and 2-propanol media is trifluoroacetic acid. This study also revealed that the strongest acid in acetonitrile medium is trifluoroacetic acid.
4. Titrations carried out in 2-propanol media showed that use of the solvents capable of forming hydrogen bonds makes the tendency of homoconjugation lower due to the formation of H-bonds of acids and/or the conjugate bases with the solvent.

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