Acids which have more than four substituents in the α or β positions should be practically unesterifiable under ordinary conditions.[12]

Finally, if considerable substitution in the α or β positions has already been made, substitution in the γ position may have some effect on esterification rate.

It has been demonstrated already that the effect of lengthening the alkyl chain of the acid portion of ethyl esters on the rate of saponification of these esters is the same as that observed in esterification.[8] In a subsequent paper it will be shown that the general effect of α and β substitution is the same for these two processes.

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[12] *Cf.* Braun and Fischer, *Ber.*, **66B**, 101 (1933).

Summary

The kinetics of the hydrogen ion catalyzed esterification of the following organic acids have been studied: β-methylvaleric acid, trimethylacetic acid, diethylacetic acid, dipropylacetic acid, dibutylacetic acid and di-isobutylacetic acid.

The velocity of esterification of β-methylvaleric acid is similar to that of isovaleric acid. Trimethylacetic acid esterifies slowly, and has a greater activation energy than normal acids. The other four acids esterify very slowly, and have a considerably increased activation energy.

The general results of esterification studies of alkyl substituted acetic acids have been discussed

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Some Unusual Hydrates of Quaternary Ammonium Salts

BY D. L. FOWLER, W. V. LOEBENSTEIN, D. B. PALL AND CHARLES A. KRAUS

Introduction

In concentrating a solution of tetra-*n*-butylammonium hydroxide for the purpose of preparing as nearly anhydrous a product as possible, it was observed that crystals appeared at room temperature in comparatively dilute solutions and that the entire mass solidified at this temperature while a large quantity of water was still present. On investigating this phenomenon further, it was found that tetra-*n*-butylammonium hydroxide forms a hydrate, containing 31 molecules of water, which melts at 30.2°. On examining solutions of tetra-*n*-butylammonium fluoride, a similar hydrate was found containing 18 molecules of water and melting at 37°. Somewhat later, tetramethyl-, tetra-*n*-propyl-, tetra-*n*-amyl- and tetraisoamylammonium hydroxides were investigated. It was found that only tetraisoamylammonium hydroxide forms a high hydrate. More recently, a considerable number of quaternary ammonium salts has been investigated in a preliminary fashion in order to determine whether they form hydrates and approximately of what composition. All the tetra-*n*-butylammonium salts having a high solubility in water were found to form hydrates, as did also tetraisoamylammonium formate, the one tetraisoamylammonium salt investigated. No salts of ions other than tetra-*n*-butylammonium and tetraisoamylammonium have been found that form high hydrates.[1]

Experimental

Method.—In determining the composition of these salt hydrates, a weighed sample of solution, which had previously been analyzed, was introduced into a suitable cell which was either cylindrical or of Erlenmeyer form and which was provided with a stopcock. The weight of the cell was known so that the composition of the solution could be obtained at any time by weighing the cell and its contents. The cell was attached to a vacuum system which was provided with a mercury manometer; an oil manometer, which had a higher sensitivity than the mercury manometer; a flask, containing water; a small pipet, graduated to 0.1 cubic centimeter; and a closed, drying tube for absorbing water vapor as desired. In most cases, the cell was attached to the apparatus by means of a short length of pressure tubing so that the contents of the cell could be shaken conveniently in determining melting points or in adjusting for pressure equilibrium. The entire apparatus was carefully exhausted so as to remove the permanent gases.

Most of the salts were prepared by titrating acids with solutions of the desired quaternary bases. The bases were prepared from the corresponding iodides by means of silver oxide. In preparing these bases, it is very essential to guard against carbon dioxide. All solutions must be made up with carbon dioxide-free water and the apparatus must

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[1] The experimental work in connection with tetra-*n*-butylammonium hydroxide and fluoride was carried out by D. L. Fowler; that of the other hydroxides by W. V. Loebenstein; that of the remaining salts by David B. Pall. Since it is not planned to continue the investigation of these hydrates at this time, the results are presented as far as they have been obtained.

be filled with carbon dioxide-free air or nitrogen. Traces of carbon dioxide are immediately absorbed by the bases to form carbonates, thus introducing an additional component which renders a study of the desired phase relations impossible.

In determining the precise composition of the hydrates, several methods were employed, depending upon the nature of the hydrate. In some cases, the initial melting point and the point of disappearance of the last crystal were observed as the temperature was slowly raised, while in others the vapor pressure curve was followed and the break point observed in passing from one phase system to another. In still other cases, the melting point curves were determined.

Tetra-*n*-butylammonium Hydroxide, $(C_4H_9)_4NOH \cdot 31H_2O$.—A quantity of tetra-*n*-butylammonium hydroxide was prepared as described under careful exclusion of carbon dioxide. Several samples of the solution were taken for analysis and the remainder was introduced into the cell and attached to the vacuum system. Melting temperatures were determined until a maximum was reached at 30.2° where the mass melted homogeneously. The weight of the cell and homogeneously melting solid was taken and the results computed as follows: weight hydrated base, 2.7681; anhydrous base, 0.8780; moles anhydrous base, 0.003386; moles water, 0.1050; moles base/moles water, 1/31.01.

$(C_4H_9)_4NOH \cdot 4H_2O$.—On withdrawing water from the hydrate described above, the entire mass liquefied and on continued withdrawal of water, a new solid phase separated. This phase had a sharp melting point at 26°. Its composition was determined as follows: wt. hydrated base, 1.1225; anhydrous base, 0.8780; moles anhydrous base, 0.003386; moles water, 0.01358; moles base/moles water, 1/4.01.

$(C_4H_9)_4NOH \cdot 2H_2O$.—On dehydration of the tetrahydrate, another solid appeared which approximated the dihydrate in composition. However, the base is not stable when this hydrate is subjected to the action of a vacuum pump. With the sample used in the preceding experiments, most of the material was lost in the course of pumping, and upon opening the tube the presence of tributylamine was detectable. Accordingly, another sample was prepared and when no perceptible liquid was left in the solid mass, the tube was weighed. The results follow: wt. hydrated base, 1.6301; anhydrous base, 1.4200; moles anhydrous base, 0.00549; moles water, 0.01167; moles anhydrous base/moles water, 1/2.12.

Tetra-*n*-butylammonium Fluoride, $(C_4H_9)_4NF \cdot 18H_2O$.—A quantity of tetra-*n*-butylammonium fluoride was prepared by titrating a solution of the hydroxide with hydrofluoric acid. After taking samples of the solution for analysis, the remainder was introduced into the cell and the composition of the hydrate determined as in the case of the hydroxide. The homogeneously melting hydrate had a melting point of 37°. The tube was weighed and the composition of the hydrate determined as follows: wt. hydrated fluoride, 8.9582; anhydrous fluoride, 3.9832; moles anhydrous fluoride, 0.01526; moles water, 0.2764; moles fluoride/moles water, 1/18.11. On further dehydration of the octadecahydrate, the whole mass liquefied and there was no evidence of the formation of any other hydrate on continued dehydration down to the pure salt.

Tetraisoamylammonium, Hydroxide, $(C_5H_{11})_4NOH \cdot 32H_2O$.—A solution of this hydroxide was prepared as described above and introduced into a cell of the Erlenmeyer form. The advantage of a container of this type is that the thickness of the liquid layer is small and the surface large and it is, therefore, easier to establish equilibrium than in the case of a narrower tube with a greater depth of liquid. To determine the composition of the hydrate in this case, pressures were observed somewhat above and somewhat below the point at which the entire mass in the tube appeared to be solid, the water content of the cell being determined after each observation. Water was then withdrawn or introduced and the range between the upper and lower pressures gradually narrowed until it approximated the composition of the hydrate. The pressures observed at 20° in millimeters of oil and the mean composition of the system in moles of water per mole of base follow:

Moles of water/base	38.5*	44.3	31.4*	34	32.9
p, mm. of oil	277	274	<228	267	264

Moles of water/base	31.4	32.3*	31.99*	32.01*
p, mm. of oil	218	266	217	>259

The pressure readings on the oil manometer may be converted to millimeters of mercury by multiplying by the factor 0.0633.

Not all the pressures as read are precise equilibrium values but observations in any one case were continued long enough to ensure that the pressures corresponded either to the equilibrium of higher or of lower pressure. The upper pressure, which is in the neighborhood of 265 mm., is the vapor pressure of the more dilute solution in equilibrium with the base hydrate, while the lower pressure of approximately 218 mm. is the pressure of the more concentrated solution in equilibrium with the same base hydrate (at 25°). The composition of all the starred values was directly determined by weighing the cell and is, therefore, accurate. The other values were determined by taking account of the amount of water introduced or removed and although sufficiently accurate for the purpose, they are not as precise as the starred values. The data for the last two values are given: wt. of hydrated base, 5.8587, 5.8602; anhydrous base, 2.0717; moles water/moles base, 31.99, 32.01. The hydrate melts homogeneously at 31°.

$(C_5H_{11})_4NOH \cdot 4H_2O$.—On dehydrating the hydrate described above, the entire mass liquefied and upon further dehydration, crystals appeared which were evidently the tetrahydrate and which melted at 57.5°. They were not entirely stable at room temperature under the action of the pump. Assuming that the base decomposes to tertiary amine, olefin and water[2] and that the tertiary amine remains behind when the hydrate decomposes, the composition of the hydrate may be determined by titrating the strong base and weighing the cell and its contents. The correction due to decomposition was of the order of 10%. Following are the results for a typical determination: mmoles. base original sample, 6.659; mmoles. base after

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(2) Meyer and Jacobson, "Lehrbuch der organischen Chemie," Vol. I, part 1, Leipzig, 1907, p. 378.

decomposition, by titration, 6.124; mmoles. base decomposed, 0.4568; wt. final product (hydrate and amine), 2.4571; wt. of amine (equivalent to 0.4568 mmoles.), 0.1038; wt. hydrated base, 2.3533; wt. anhydrous base (6.124 mmoles.), 1.9254; wt. water, 0.4279; mmoles. water, 23.75; moles base/moles water, 1/3.88.

Tetra-*n*-amylammonium Hydroxide, $(C_5H_{11})_4NOH \cdot 4H_2O$.—With this base there was found no evidence of the existence of a high hydrate. A solid ultimately was formed whose composition approximated that of the tetrahydrate and which proved unstable under the action of the pump. Making corrections for the amount of the base decomposed, and assuming that the free amine resulting was not lost, the following results were obtained: mmoles. original base, 8.273; mmoles. after decomposition, 7.676; mmoles. of water in final hydrate, 29.5; moles base/moles water, 1/3.9.

Tetramethylammonium Hydroxide, $(CH_3)_4NOH \cdot 5H_2O$.—On concentrating a solution of this base, the first hydrate that appeared was the already known pentahydrate.[3] The results follow: wt. anhydrous base, 0.6402; hydrated base, 1.2590; hydrate water, 0.6188; moles base/moles water, 1/4.9.

Tetra-*n*-propylammonium Hydroxide.—Although the existence of a heptahydrate of this base is reported in the literature,[4] all attempts to obtain a crystalline product with this base failed. In one case, the liquid having a composition closely approximating that of the heptahydrate was left at sub-zero temperature overnight without the appearance of crystals. On further concentrating the solution, the product decomposed rather suddenly at room temperature.

Ethyltri-*n*-butylammonium Hydroxide.—The behavior of a solution of this base resembled that of tetra-*n*-propylammonium hydroxide on concentration. No crystals could be obtained and when the concentration of the solution approximated that of three moles of water per mole of base, decomposition occurred.

Tetra-*n*-butylammonium Oxalate, $[(C_4H_9)_4N]_2C_2O_4 \cdot 38H_2O$.—The salt was prepared by metathesis of silver oxalate and tetrabutylammonium iodide. It was purified by recrystallizing three times from water at 0°. The composition of the hydrate was determined by the vapor pressure method; three determinations gave the following values for the number of moles of water per mole of salt: 37.5, 37.6, 37.9. The hydrate melted between 20 and 25°.

Tetra-*n*-butylammonium Formate, $(C_4H_9)_4NCHO_2 \cdot 33H_2O$.—This salt has a very flat melting point curve with a maximum near 12.5° and 33 moles of water. The composition was also checked by the vapor pressure method which yielded the same value but the difference between the upper and the lower vapor pressures was extremely small.

Tetra-*n*-butylammonium Bromide, $(C_4H_9)_4NBr \cdot 26H_2O$.—The salt was prepared by digesting tetra-*n*-butylammonium iodide with an excess of silver bromide in aqueous solution. After evaporating the solution, the salt was recrystallized from ethyl acetate, melting point 113°. The melting point curve of solutions of this salt is much less flat than that of the formate and has a maximum at 14.5° at a composition corresponding to 26 molecules of water.

Other Hydrated Salts.—Rough determinations were made with some other salts. Tetraisoamylammonium formate yielded a product melting at 15–20° with a composition in the neighborhood of 50 moles of water per mole of salt. Tetra-*n*-butylammonium acetate yielded a hydrate melting at 10–15° and containing 60 molecules of water. Tetra-*n*-butylammonium propionate yielded a hydrate melting at 17° and containing 50 molecules of water. Tetra-*n*-butylammonium benzoate yielded a hydrate melting at 3.5° and containing approximately 35 molecules of water. Tetra-*n*-butylammonium nitrate yielded a hydrate melting at 5.8° and containing 27 molecules of water. Tetra-*n*-butylammonium chloride yielded a hydrate melting at 15° and containing 30 molecules of water. Tetra-*n*-butylammonium sulfate and tetra-*n*-butylammonium chromate both yielded hydrates but their approximate composition was not determined.

Tetra-*n*-butylammonium thiocyanate, picrate and cyanide were found to be difficultly soluble in water and yielded no hydrates. Tetra-*n*-propylammonium formate, tetra-*n*-amylammonium formate, tetra-*n*-amylammonium acetate, methyltri-*n*-butylammonium formate and propyltri-*n*-butylammonium formate yielded no hydrates. Tetra-*n*-propylammonium fluoride deposited a solid from fairly concentrated aqueous solution, apparently in anhydrous form.

Summary

The highly soluble salts of tetra-*n*-butylammonium and tetraisoamylammonium ions quite generally form hydrates containing above 15 molecules of water and having relatively high melting points. The following hydrates have been accurately determined: $(n\text{-}C_4H_9)_4NOH \cdot 31H_2O$, m. p. 30.2°; $(n\text{-}C_4H_9)_4NF \cdot 18H_2O$, m. p. 37°; $(i\text{-}C_5H_{11})_4NOH \cdot 32H_2O$, m. p. 31°; $[(n\text{-}C_4H_9)_4N]_2C_2O_4 \cdot 38H_2O$, m. p. 20–25°; $(n\text{-}C_4H_9)_4NCHO_2 \cdot 33H_2O$, m. p. 12.5°; $(n\text{-}C_4H_9)_4NBr \cdot 26H_2O$, m. p. 14.5°.

Other salts yielding high hydrates whose composition and melting points have been less accurately determined are the following: $(i\text{-}C_5H_{11})_4NCO_2 \cdot 50H_2O$, m. p. 15–20°; $(n\text{-}C_4H_9)_4NCH_3CO_2 \cdot 60H_2O$, m. p. 10–15°; $(n\text{-}C_4H_9)_4NC_2H_5CO_2 \cdot 50H_2O$, m. p. 17°; $(n\text{-}C_4H_9)_4NC_6H_5CO_2 \cdot 35H_2O$, m. p. 3.5°; $(n\text{-}C_4H_9)_4NNO_3 \cdot 27H_2O$, m. p. 5.8°; $(n\text{-}C_4H_9)_4NCl \cdot 30H_2O$, m. p. 15°. Tetra-*n*-butylammonium sulfate and tetra-*n*-butylammonium chromate both yield high hydrates but their approximate composition was not determined.

Higher hydrates could not be found in the case of tetramethylammonium hydroxide, tetra-*n*-propylammonium hydroxide, tetra-*n*-amylammonium hydroxide and ethyltri-*n*-butylammonium hydroxide.

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[3] Walker and Johnston, *J. Chem. Soc.*, **87**, 958 (1905).

[4] Crichton, *ibid.*, **91**, 1796 (1907).