[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Acetolysis of Esters

BY SAUL G. COHEN[1]

The reactions of carboxylic esters with water and alcohols in the presence of acidic and basic catalysts have been studied in great detail, and the mechanisms of these reactions are fairly well understood in broad outline.[2] However, the reactions of esters with carboxylic acids, which may be considered as formally similar but less basic hydroxylic solvents have received less attention. The acidolysis of esters leads to ester interchange reactions in which the acid parts of the esters are exchanged.

$$R'COOR + R''COOH \rightleftharpoons R''COOR + R'COOH$$

Examples of this interchange may be found in the reactions of a series of esters with stearic acid,[3] in the acetolysis of esters of *p*-methoxybenzhydrol and of substituted allylic alcohols,[4] and in the acetolysis of esters of primary and secondary alcohols.[5]

Previous attempts to effect the acidolysis of esters of tertiary alcohols have led only to their decomposition.[3] We also found that, when *t*-butyl benzoate was boiled in acetic acid in the absence of added catalysts, decomposition took place. In one experiment, after twenty hours of boiling, 17% of *t*-butyl benzoate, and benzoic acid, accounting for 87% of the remainder, were recovered. *t*-Butyl acetate, the product of ester interchange, was obtained in only 8.5% yield.

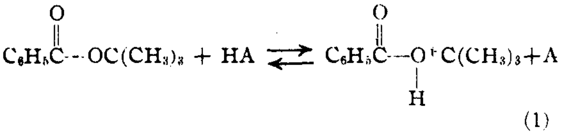
The desired ester interchange was readily obtained when the reaction was carried out at room temperature in the presence of a catalyst. A solution of *t*-butyl benzoate and *p*-toluenesulfonic acid in acetic acid was allowed to stand for two days, and was then treated with potassium acetate and fractionated. *t*-Butyl benzoate was recovered (25%), and *t*-butyl acetate, benzoic acid and isobutene were obtained in 65, 61 and 6.5% yield, respectively, based on consumed *t*-butyl benzoate. When this reaction was carried out at the boiling point, acetolysis was rapid, being 76% complete, in two and one-half hours, but no *t*-butyl acetate was found. The formation of this product depended on a low reaction temperature and probably was not due to an acid catalyzed addition of acetic acid to isobutene.

When a solution of *i*-propyl benzoate in acetic acid, containing *p*-toluenesulfonic acid, was boiled for twenty-four hours, 69.7% of the ester was recovered, and benzoic acid and *i*-propyl acetate, accounting for 57 and 58% of the remainder were isolated. Propylene was not detected. The acetolysis of *i*-propyl benzoate was much slower than that of *t*-butyl benzoate, and it was not complicated by olefin formation. When ethyl and methyl benzoates were tested under the same conditions, no evidence of acetolysis was found, and the starting materials were recovered in 88% yield.

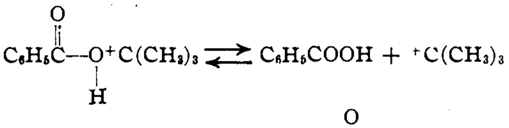
This marked relative sensitivity of esters of *t*-butyl alcohol to carboxylic acids may in part account for the fact that all attempts to resolve tertiary alcohols through their acid phthalates have failed.

Thus, we find that, in the acid catalyzed acetolysis of esters, the tertiary alcohol ester is most reactive, the secondary is less reactive, and, under comparable conditions, the primary alcohol esters are inert. In reactions which proceed by coordination of a basic reagent or a hydroxylic solvent at the carbonyl carbon atom of an ester the inverse order of reactivity is found. Thus, in the base-catalyzed alcoholysis and hydrolysis of esters, and in the acid catalyzed hydrolysis and alcoholysis of esters of primary and secondary alcohols, the esters of primary alcohols are most reactive.[2] The order of reactivity which we find in the acid catalyzed acetolysis is the same as that for the solvolytic reactions of the corresponding alkyl halides,[6a] or for the formation of the alkyl carbonium ions.[6b] It is found in no other reactions of carboxylic esters with hydroxylic solvents and indicates that a mechanism is operative which is not generally found in the other reactions of esters.

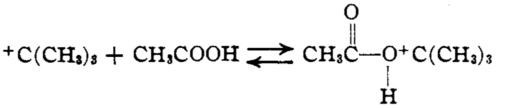
The reactions which are involved in the acid catalyzed acetolysis may be depicted adequately by the following mechanism, which seems preferable to that of Sowa,[5] in view of the observed order of reactivity.



$$C_6H_5\overset{O}{\overset{\|}{C}}-OC(CH_3)_3 + HA \rightleftharpoons C_6H_5\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{O^+}}C(CH_3)_3 + A \qquad (1)$$



$$C_6H_5\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{O^+}}C(CH_3)_3 \rightleftharpoons C_6H_5COOH + {}^+C(CH_3)_3 \qquad (2)$$



$${}^+C(CH_3)_3 + CH_3COOH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{O^+}}C(CH_3)_3 \qquad (3)$$

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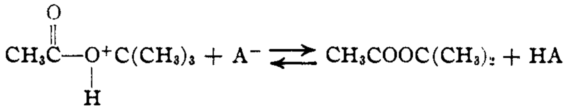
[2] (a) Day and Ingold, *Trans. Faraday Soc.*, **37**, 686–705 (1941); (b) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 355–359; (c) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, pp. 394–402.

[3] Barkenbus, Roswell and Mitts, THIS JOURNAL, **62**, 1251 (1940). This article contains references to earlier work.

[4] Balfe, Doughty, Kenyon and Poplett, *J. Chem. Soc.*, 605 (1942); Balfe, Hills, Kenyon, Phillips and Platt, *ibid.*, 556 (1942).

[5] Sowa, THIS JOURNAL, **60**, 654 (1938).

[6] (a) Hammett, *loc. cit.*, p. 170; (b) Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).



$$CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{O^+}}C(CH_3)_3 + A^- \rightleftharpoons CH_3COOC(CH_3)_3 + HA \qquad (4)$$

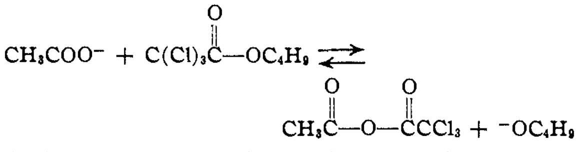
$$^+C(CH_3)_3 + A^- \rightleftharpoons CH_2{=}C(CH_3)_2 + HA \qquad (3a)$$

In equation (1), the acid HA may be the solvated proton, $CH_3COOH_2^+$, or a toluenesulfonic acid molecule or an acetic acid molecule. The ionization (2) occurs at room temperature in the tertiary ester but only at higher temperatures in the case of the secondary ester. Reaction (3a), the alternative reaction of the tertiary carbonium ion intermediate, involving the rupture of a carbon hydrogen bond, may well have a somewhat higher activation energy than reaction (3) and be favored at higher temperatures.[7]

This mechanism is similar to that which was suggested for the acid catalyzed hydrolysis and alcoholysis of esters of tertiary alcohols.[8] In the acetolysis, it is also found in the reactions of esters of secondary alcohols, the formation of the secondary carbonium ion comparing favorably in rate with alternative feasible reaction course, the addition of a solvent molecule to the carbonyl group of the ester. This addition, leading to the intermediate formation of an acid anhydride, would be expected to be quite slow because of the low basicity of the solvent, acetic acid. In the acid hydrolysis of esters of secondary alcohols the addition of a water molecule to the carbonyl group is relatively fast because of the greater basicity of water and reaction by this mechanism predominates.

An example of a base catalyzed acetolysis of an ester was found. Ethyl butyrate was found to undergo no reaction when boiled for eight hours in acetic acid in the presence of potassium acetate. However, when butyl trichloroacetate was treated similarly, acetolysis occurred. Starting material (55%) was recovered, and butyl acetate, accounting for 65% of the remainder was obtained.

This reaction may proceed by displacement of the trichloroacetate ion by attack by the acetate ion on the alkyl carbon atom, much as a toluenesulfonate group may be displaced.[9] Such a reaction may be favored because of the strength of trichloroacetic acid. Alternatively, the reaction may involve attack on the carbonyl carbon atom by an acetate ion, forming a mixed anhydride of acetic and trichloroacetic acids as an intermediate.



$$CH_3COO^- + C(Cl)_3\overset{O}{\overset{\|}{C}}-OC_4H_9 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}CCl_3 + {}^-OC_4H_9$$

Such a reaction may be facilitated in this case because of activation of the carbonyl group by the trichloromethyl group. More will be known about the mechanism when the reactions of optically active secondary octyl trichloroacetate will have been studied.

Experimental

Acetic Acid–Acetic Anhydride Solvent.—A solution of 20 cc. of Eastman Kodak Co. acetic anhydride in 350 cc. of reagent acetic acid was boiled for two hours and allowed to stand for at least one day before use.

Catalyst Solution.—A portion of catalyst solution was prepared by boiling a solution of 2 g. of *p*-toluenesulfonic acid in 10 cc. of acetic acid and 10 cc. of acetic anhydride for two and one-half hours.

***t*-Butyl benzoate** was prepared in 86% yield by the method of Norris and Rigby,[10] b. p. 91.3° (7.5 mm.), n^{20}_D 1.4910.

Acetolysis of *t*-Butyl Benzoate.—(1) A solution of 40.5 g. of *t*-butyl benzoate in 57 g. of acetic acid–acetic anhydride was boiled for twenty hours. The material boiling over a range to 74° (139 mm.) was collected and from it was obtained *t*-butyl acetate, b. p. 98–102°, n^{25}_D 1.3840, 1.85 g., 8.5% yield. From the residue there were recovered *t*-butyl benzoate, b. p. 98° (11 mm.), 7 g., 17% yield, and benzoic acid, m. p. and mixed m. p. 121–122°, 19.9 g., 87% yield based on unrecovered ester.

(2) A solution of 15.7 g. of *t*-butyl benzoate and one-half of a portion of toluenesulfonic acid catalyst solution in 30.5 g. of acetic acid was prepared. A part of this was boiled for two and one-half hours and fractionated. No *t*-butyl acetate was detected, and benzoic acid was obtained in 76% yield. The remainder of the original solution was allowed to stand for two days at room temperature. One gram of potassium acetate was added and the solution was fractionated. *t*-Butyl benzoate, the starting material was recovered in 25% yield, b. p. 104° (13 mm.). A small quantity (0.25 g.) of a liquid with the characteristic odor of isobutene, boiling below 0° and above −20° was found. Benzoic acid, m. p. and mixed m. p. 121.5–122.5°, and *t*-butyl acetate, b. p. 97.6–100.6°, n^{25}_D 1.3839 were obtained in 61 and 52.5% yield, respectively. The content of *t*-butyl acetate in an intermediate fraction raised the estimated yield of this product to 65%.

Acetolysis of *i*-Propyl, Ethyl and Methyl Benzoates.—The esters obtained from Eastman Kodak Co., were dried and distilled. The boiling points were 106.5–107.5° (21 mm.), 103° (22 mm.), and 91° (21 mm.), respectively, and the refractive indices were n^{25}_D 1.4924, n^{20}_D 1.5055, and n^{21}_D 1.5174, respectively.

A solution of 30 g. of *i*-propyl benzoate and a portion of the catalyst solution in 62 g. of acetic acid–acetic anhydride was boiled for twenty-four hours. No propylene was detected in a dry-ice trap. Fractionation, and bicarbonate extraction of the benzoic acid led to the recovery of *i*-propyl benzoate, b. p. 107° (22 mm.), n^{25}_D 1.4916, 20.9 g., *i*-propyl acetate, b. p. 87.6–90.6°, n^{25}_D 1.3758, 3.3 g. and benzoic acid, 4.07 g.

When ethyl and methyl benzoates were treated similarly, neither benzoic acid nor ethyl or methyl acetates were recovered. The starting materials were obtained in 88% yield.

***n*-Butyl trichloroacetate** was prepared by the method of Palomaa, Salmi and Korte,[11] b. p. 97–99° (19 mm.), n^{25}_D 1.4496, 89% yield.

Acetolysis of Butyl Trichloroacetate.—A solution of 0.465 mole of freshly fused potassium acetate, 5 cc. of acetic anhydride, and 0.465 mole of butyl trichloroacetate in 100 cc. of acetic acid–acetic anhydride was warmed on the water-bath for eight hours. Part of the solution was boiled out, 103 g., boiling to 123°. The distillate and residue were each washed with sodium bicarbonate solution and with water, extracted with ether, dried and fractionated. Butyl trichloroacetate was recovered, 0.255 mole, 94° (17 mm.), 55%, and butyl acetate was obtained,

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(7) Hughes and Ingold, *Trans. Faraday Soc.*, **39**, 669 (1942).

(8) Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

(9) Phillips, *J. Chem. Soc.*, **123**, 44 (1923).

(10) Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

(11) Palomaa, Salmi and Korte, *Ber.*, **72**, 797 (1939).

b. p. 125.6–126.9°, n^{20}_D 1.3940, 65.7% yield based on unrecovered butyl trichloroacetate.

Treatment of butyl trichloroacetate with acetic acid at 115° for nine hours in the presence of *p*-toluenesulfonic acid led to no products of acetolysis. Butyl trichloroacetate was recovered in 93% yield.

A solution of 56 g. of ethyl butyrate, 48 g. of fused potassium acetate and 5 cc. of acetic anhydride in 100 cc. of acetic acid–acetic anhydride was boiled for eight hours. No evidence of ethyl acetate was found. Ethyl butyrate was recovered, 119–120.5°, n^{20}_D 1.3923, 48.3 g., 86%.

Summary

The results of a qualitative study of the effect of structure of the alkyl group on the acetolysis of esters are reported. In the acid catalyzed acetolysis of esters of benzoic acid, the *t*-butyl ester was found to be quite reactive, the *i*-propyl ester, less reactive, and the ethyl and methyl esters, inert under comparable conditions. In the base-catalyzed acetolysis, a typical aliphatic ester was found to be inert, while butyl trichloroacetate was reactive. These reactions lead to ester interchange by the exchange of the acid parts of the esters. The mechanisms of these reactions are discussed.

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The Heat Capacity of Potassium Dihydrogen Phosphate from 15 to 300°K. The Anomaly at the Curie Temperature

BY C. C. STEPHENSON AND J. G. HOOLEY[1]

The heat capacity of KH_2PO_4 is of particular interest since this salt has unusual dielectric properties at low temperatures. Busch[2] found that KH_2PO_4 is similar to Rochelle salt in that it has an electric Curie point: below this temperature, the salt is spontaneously polarized along the *c*-axis. The electric properties of Rochelle salt, KH_2PO_4 and KH_2AsO_4 are very similar to the magnetic properties of ferromagnetic substances,[3] and anomalies in the heat capacities of these substances are to be expected near the Curie points. The recent investigations of the heat capacity of Rochelle salt by Hicks and Hooley[4] and by Wilson[5] have shown that any anomalous increase in the heat capacity of this salt at the Curie points must be less than one per cent. of the total heat capacity. Professor Hans Mueller called our attention to the fact that KH_2PO_4 should have an easily detectable anomaly at the Curie point since this crystal has a much larger permanent polarization than Rochelle salt, and at his suggestion we have measured the heat capacity of this substance.

While these measurements were being made, a theory of the transition, derived from a consideration of the arrangement of the hydrogen bonds in the crystal, was proposed. The entropy change predicted from theory is in agreement with the experimental value reported in this paper. Confirmation of the theoretical entropy change has also been obtained from a later study of the transitions in KH_2AsO_4 and $NH_4H_2PO_4$.

Material.—The salt was of C. P. reagent quality and contained less than 0.03% impurities[6] other than water. The salt was dried over phosphorus pentoxide and in vacuum; the heat capacity measurements in the neighborhood of the ice point show the absence of water. The percentage loss of weight on ignition to KPO_3 was 13.29; theoretical, 13.24. The material used for the measurements consisted of small crystals approximately 1 × 0.2 × 0.2 mm.

All measurements were made on a single calorimeter loading of 104.923 g. *in vacuo*, or 0.7710 mole. The molecular weight of KH_2PO_4 was taken as 136.09.

Method.—The apparatus and method of measurement have been described previously.[7] It is of interest that the calorimeter is the same as that used by Hicks and Hooley[4] for their measurements on Rochelle salt.

The temperatures were measured by means of a platinum–rhodium resistance thermometer-heater which had been calibrated previously against a helium gas thermometer.[8] The ice-point resistance of this thermometer was measured during this investigation, and no appreciable departure from the original calibration value was found.

At the conclusion of these measurements and corresponding measurements on KH_2AsO_4, the heat capacity of the empty calorimeter was redetermined. The new measurements are somewhat better than the previous ones due to improvements in the apparatus and are within the limits of accuracy of the older measurements.

The resistance thermometer and thermocouple readings were taken on a new Wenner potenti-

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[1] Royal Society of Canada Fellow. Present address, University of British Columbia, Vancouver, Canada.

[2] G. Busch, *Helv. Phys. Acta*, **11**, 269 (1938).

[3] For a review of recent work, see H. Mueller, "Annals of the New York Academy of Sciences," XL, 321 (1940).

[4] J. F. G. Hicks and J. G. Hooley, THIS JOURNAL, **60**, 2994 (1938).

[5] A. J. C. Wilson, *Phys. Rev.*, **54**, 1103 (1938).

[6] Prof. S. G. Simpson of the Analytical Division of the Chemistry Department, M.I.T., kindly performed the quantitative analyses.

[7] J. F. G. Hicks, THIS JOURNAL, **60**, 1000 (1938).

[8] R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).