was accomplished with 200 g. of Raney nickel and 500 cc. of alcohol, to yield 7.2 g. (0.05 mole, 77%) of ethyl hydrocinnamate, b. p. 113–115° at 10 mm., $n^{20}\text{D}$ 1.487, amide m. p. 99–100°.[14,15]

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[14] J. Bruhl, *Ann.*, **200**, 192 (1879).

[15] S. King and F. McMillan, THIS JOURNAL, **68**, 525 (1946).

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The Relation between Steric Hindrance and Ionization Constant of Certain Acids

BY H. L. LOCHTE AND PATRICIA BROWN[1]

In a number of cases aliphatic and alicyclic carboxylic acids which are sterically hindered, as indicated by a very low rate of esterification under ordinary Fischer esterification conditions, have been found to be weaker than unhindered acids of the same molecular weight and type. In the few instances in which the ionization constants of hindered alicyclic or aliphatic acids have been determined the acids have been tertiary acids, *i. e.*, the carboxyl group was attached to a tertiary carbon atom. These were found to be about one K_a unit weaker than unhindered acids of the same type[2,3] One such acid, campholic, may be separated from the isomeric unhindered isocampholic acid by taking advantage of the fact that campholic acid may be liberated from its sodium salt solution by carbonic acid and so has been considered to be a much weaker acid.[4]

Since highly hindered acids in which the carboxyl group is attached to a secondary carbon are now available in *cis*- and *trans*-2,2,6-trimethylcyclohexanecarboxylic acids it seemed worthwhile to determine, in a single series of measurements, the ionization constants of a number of unhindered, hindered tertiary and the two hindered secondary acids mentioned, all of the acids, except benzoic, being alicyclic in nature.

Apparatus and Method

Several of the acids are not sufficiently soluble in water to permit its use as solvent in this series of measurements which were to be made under as nearly identical conditions as possible. It was found that a 25% solution of dioxane in water can be used as solvent with all of the acids. Peroxides were removed from Eastman Kodak Co. dioxane by distillation from powdered iron and ferrous sulfate. The distillate gave no iodide test for peroxides and was redistilled as the binary azeotrope before each series of determinations and then diluted to 25% with carbon dioxide-free water.

It was decided to use the method of Kumler[5] using glass electrodes for the *p*H determinations after preliminary experiments indicated that the hydrogen electrode was not satisfactory in the dioxane solution used. To avoid electrical interferences in the glass electrode measurements, water from a thermostat operating at 25.0 ± 0.1° was circulated through a quart vacuum bottle in which the titration vessel consisting of a large Pyrex test-tube was suspended. The Beckman external glass electrode–saturated calomel electrode system and a glass capillary were hung in the large test-tube. Stirring was effected by hydrogen gas bubbled through the capillary.

It was found that erratic results were obtained in the *p*H measurements on standard buffers as well as in K_a value determinations on pure benzoic acid using Kumler's formula unless certain precautions were taken in conditioning the glass electrodes.

Dioxane solution was used to rinse the electrodes between titrations of different samples of the same acid. On completion of readings on any one acid the electrodes were rinsed with distilled water and allowed to remain in water for at least an hour before use with a different acid.

Three samples, weighed on a semi-micro balance to 0.01 mg., were placed in titration vessels and 70 ml. of 25% dioxane–water solution added to each. The vessels were heated in a water-bath to dissolve the samples and allowed to cool to room temperature. Before use the electrodes were rinsed with the dioxane solution, placed in the titration cell and left in contact with the solution for 15 minutes before any measurements were taken. After this waiting period the exact volume of sodium hydroxide solution required for 0.333 neutralization of the acid was added from a micro buret and the *p*H determined after stopping the hydrogen stream through the capillary. Similar readings were obtained after 0.500 and 0.666 equivalent of sodium hydroxide had been added. The three samples yielded then data for nine K_a values for each acid. In the typical case of cyclohexanecarboxylic acid these values were 0.182, 0.182, 0.175; 0.173, 0.181, 0.167; and 0.162, 0.178, 0.167 × 10^{-5}. The K_a values listed in Table I represent averages of the three averages obtained from such data.

TABLE I

Acid	M. p., °C.	K_a × 10^{-5}
Benzoic	121–122	1.17
Cyclohexanecarboxylic	30[a]	0.174
Cyclopentanecarboxylic	b. p. 215–216[b]	.126
1-Isopropylcyclohexanecarboxylic	103–104[c]	.0362
1,2,2-Trimethylcyclopentanecarboxylic	191–192[d]	.0348
1,2,2,3-Tetramethylcyclopentanecarboxylic	106–107[e]	.0353
"*trans*"-2,2,6-Trimethylcyclohexanecarboxylic	82–83[f]	.106
"*cis*"-2,2,6-Trimethylcyclohexanecarboxylic	73–74[g]	.0241

[a] Prepared *via* Grignard reaction; b. p. 230–233°. [b] Prepared by Ney, THIS JOURNAL, **65**, 770 (1943); refractionated. [c] Prepared by Shive, *ibid.*, **63**, 2979 (1941); recrystallized. [d] Isolated from petroleum and purified by Hancock, *ibid.*, **61**, 2448 (1939); recrystallized. [e] Prepared by alkali fusion of camphor by Stallings, Ph.D. Thesis, University of Texas, 1949. [f] Isolated from petroleum and purified by Horeczy, THIS JOURNAL, **64**, 385 (1942); recrystallized. [g] Prepared by Shive, *ibid.*, **64**, 385 (1942); recrystallized.

The unexpectedly large differences between K_a values of the second and third acids and the very large difference between the "*cis*" and "*trans*" acids are far outside of experimental error and remain unexplained. They may indicate that glass electrode *p*H measurements in dioxane–water solutions even though reproducible, should not

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[1] Presented in partial fulfillment of requirements for the degree of Master of Arts, the University of Texas, 1949.

[2] Ostwald, *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

[3] Guha and Bhattacharyya, *J. Ind. Chem. Soc.*, **21**, 333–337 (1944).

[4] Wallach, *Ann.*, **369**, 74 (1909); Elbs and Tölle, *J. prakt. Chem.*, [2] **32**, 622 (1885).

[5] Kumler, THIS JOURNAL, **60**, 863 (1938).

be used to compare acid strengths until after further investigation.

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Acetylation of Starch

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It is stated that starch must be pregelatinized before it can be converted to the triacetate through the action of pyridine–acetic anhydride.[1,2] We have found that, although raw corn starch is somewhat resistant to the action of these reagents at 100°, treating it with refluxing (115°) pyridine for about an hour permits acetylation without prior gelatinization.[3] These activation conditions allow complete acetylation of corn starch but only partial acetylation of potato or tapioca starch.

TABLE I

ACETYLATION IN PYRIDINE–ACETIC ANHYDRIDE

Pyridine pretreatment[a]	Time to clear at 100°,[b] hr.	Total time, hr.	% yield	Acetyl[c]
None	>10	22.5	98.5	44.7
Reflux 1 hr.	1.75	2	97.7	44.8
Reflux 1 hr.	1	2	98.2	44.6
Azeotropically dried	1	2	97.2	44.8

[a] The first two samples contained 11% moisture and the third was dried *in vacuo* to constant weight. [b] Microscopic examination at 600 × for disappearance of granules or granule fragments from the mixture. [c] By saponification, dry basis; theory for triacetate, 44.8%.

Differences in reactivity of various starch species appear to be related to granule size, starches of larger granule size being less reactive.[4]

Esterification of untreated starch at 115° is sluggish and pretreatment at 100° is not appreciably effective. Drying of activated granules to a pyridine content of 7% (which is held very tenaciously) makes them non-reactive.

The pyridine pretreatment does not gelatinize the starch; the granules are still birefringent and are swollen only about 50% by volume. "Horny starch" (made by drying an aqueous starch paste) is quite unreactive but may also be activated by this method. The ease of activation increases as the horny starch is more finely ground. We found no difference in the reactivity of defatted and non-defatted corn starch. Several lots of commercial corn starch showed no noticeable difference in ease of activation and acetylation.

In general, other common organic bases such as α-picoline, pyrrole, triethylamine, benzyldimethylamine or piperidine, have much less or no activating effect.

Acetates prepared from activated granules do not dissolve completely in solvents such as chlorinated hydrocarbons or cyclohexanone, which are normally good solvents for starch acetates. Numerous gel particles are still visible after the suspension has been shaken for several days.

By replacement of part of the pyridine by a non-solvent, such as heptane or diamyl ether (which require substantially longer reaction times), it is possible to prepare acetates that retain the original granule form. The effect of several variables on the partial acetylation of starch in the granule form is given in Table II.

TABLE II

ACETYLATION OF STARCH GRANULES IN PYRIDINE–HEPTANE

Reflux in pyridine,[a] hr.	Ac_2O,[b] moles	Acetyl, %	Recovery, %
0	3	3.1	98.9
1	3	32.8	99.8
0	4	31.4	99.1
1	4	39.0	99.3
0	4	<1	98.6
1	4	37.6	100.4

[a] All starch samples contained 10.8% moisture except the last two which were dried *in vacuo* to constant weight. [b] Sufficient excess anhydride was used to react with the moisture in the air-dried starches.

A monoacetate of corn starch granules was made in diamyl ether. This product, which still showed the typical birefringence, consumed only 0.58 mole of periodate for each acetylated anhydroglucose unit. Since starch-6-acetate would consume one mole, this shows that the hydroxyl group on carbon six did not acetylate selectively.

Experimental

Starch Triacetate.—Twenty-five grams of defatted, air-dried corn starch (moisture about 11%) was pretreated as outlined in Table I. The acetylation was carried out in 250 cc. of pyridine and 66 cc. (50 cc. in the case of dried starch) of acetic anhydride at 100°. After the stated times had elapsed, the acetate was precipitated in 3 volumes of ethanol in a high-speed blender. The acetate was washed with ethanol, dried in a vacuum desiccator and equilibrated at 50% relative humidity. All preparations adsorbed about 2% moisture.

Acetylation of Granules.—A mixture of 20.0 g. of corn starch (10.8% moisture) and 40 cc. of pyridine was heated to reflux for one hour. One hundred sixty cc. of heptane and 42 or 53 cc. (3 or 4 molar equivalents, resp., plus that equivalent to moisture in the starch) of acetic anhydride was added and the mixture was stirred and refluxed (96–97°) for three hours. The product was filtered, washed thoroughly with ethanol and dried at 50% relative humidity. In the experiments with oven-dried starch 42 cc. of acetic anhydride (4 molar equivalents) was used.

Starch Granule Monoacetate.—Twenty grams of air-dried, defatted corn starch was heated with 100 cc. of pyridine and 60 cc. of distillate was removed—the final 30 cc.

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(1) J. W. Mullen II and E. Pacsu, *Ind. Eng. Chem.*, **34**, 1209 (1942).

(2) R. L. Whistler, "Advances in Carbohydrate Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1945, p. 285.

(3) It is noted, as this article goes to press, that H. Sanders and T. S. W. Gerwitz (Abstracts of Papers, 117th Meeting, American Chemical Society, Detroit, April 1950) have obtained what appear to be somewhat parallel results with the propionylation of starch. We have also found that granules may be butyrylated.

(4) R. Lohmar, J. W. Sloan and C. E. Rist, THIS JOURNAL, in press. See also G. K. Hughes, A. K. Macbeth and F. L. Winzor, *J. Chem. Soc.*, 2026 (1932).