[CONTRIBUTION NO. 90 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Kinetics of Esterification and of Catalytic Hydrogenation of the Furoic and Furanacetic Acids

BY HILTON A. SMITH, JAMES B. CONLEY AND W. HOLMES KING

The two isomeric furoic acids and the two isomeric furanacetic acids have been obtained in pure form, and their rates of acid-catalyzed esterification measured at temperatures of 25, 35, 45 and 55°. The furanacetic acids esterify several hundred times faster than the furoic acids; the activation energies for the furoic acids are around 16,000 cal./mole while those for the furanacetic acids are around 10,000. These differences are caused by conjugation between the furyl and carboxyl groups. When the same acids are hydrogenated in acetic acid solution over platinum catalyst, all undergo hydrogenation at approximately the same rate, and the activation energies are all of the order of 8000–9000 calories per mole. Thus there is no evidence of conjugation between the carboxyl and furyl groups. Apparently the resonance is destroyed when the acids are adsorbed on the catalyst surface.

In a previous communication, evidence was presented to show that the resonance of the benzene molecule is destroyed when it is absorbed on the surface of a platinum catalyst.[1] Further evidence is found when one compares the kinetics of acid-catalyzed esterification of benzoic and phenylacetic acids with the kinetics of catalytic hydrogenation of these materials. When these acids are esterified, the conjugation between the carboxyl and phenyl groups in benzoic acid affects the rate constant, the energy of activation, and the relative entropy of activation. In phenylacetic acid, these groups are not conjugated, and hence this acid behaves much like the normal aliphatic acids.[2] When the rates of hydrogenation of the phenyl group in these two acids were determined, it was found that they were essentially the same.[3] Apparently the conjugation between the two groups is destroyed on the catalyst and, since the benzene ring is hydrogenated, it is apparently the conjugation within the phenyl group which is primarily affected.

It seemed of interest to check this observation on another system, and the furan nucleus was chosen. A general study of the hydrogenation of furan and substituted furans has already been reported.[4] This work included 2-furoic acid as well as methyl-substituted furans.

Experimental

2-Furoic acid was obtained from the Eastman Kodak Company. It was twice recrystallized from water. 2-Furanacetic acid was prepared by the method of Plucker and Amstutz.[5] The starting material for the preparation of 3-furoic acid was the sodium salt of oxalacetic ester. This was treated with bromine and then sulfuric acid to form the ethyl ester of furantetracarboxylic acid.[6] The ester was then converted to the tetracarboxylic acid using the directions of Kirkpatrick.[7] The tetracarboxylic acid was decarboxylated as follows: A mixture of 122 g. of the crude acid, 250 ml. of quinoline and 50 g. of copper powder was refluxed and the CO_2 evolved collected over water saturated with CO_2. When the equivalent of 2.4 moles[8] of gas per mole of acid had been collected (about 2 hours) the reaction mixture was allowed to cool. It was filtered, treated with an excess of 10% sodium hydroxide, refiltered, washed with ether and acidified with dilute hydrochloric acid. The acid solution was treated with four portions of ether, the extract dried, and the ether removed by evaporation. The crude 3-furoic acid was purified by subliming at 80° under a pressure of less than one mm. A yield of 24.5 g. of pure product was obtained; m.p. 121.4–122.2° (reported[6] 122–123°). The residue remaining after sublimation was assumed to be furandicarboxylic acid, and was again decarboxylated until one mole of carbon dioxide was evolved. An additional 6.1 g. of the 3-furoic acid was obtained making a total yield of 30.6 g. (55%).

There is no previously reported synthesis of 3-furanacetic acid. It was prepared as follows: 3-furoyl chloride was prepared from the 3-furoic acid by the method of Gilman and Burtner.[9] A solution of 28 g. of diazomethane in 1000 ml. of ether was cooled to 0° in an ice-bath. To this was added with stirring a solution of 23 g. of 3-furoyl chloride in 100 ml. of ether. The temperature was kept below 7° during the addition. The reaction mixture was allowed to warm to room temperature and stand overnight after which the ether was evaporated in a stream of air, and the product dried in a vacuum desiccator. The crude diazomethyl ketone (23 g.) was dissolved in 150 ml. of dry methanol, and the solution heated to about 60°. To the stirred solution was added dropwise a solution of 5 g. of silver benzoate in 25 ml. of triethylamine.[10] The nitrogen evolved was collected until about 80% of the theoretical amount of gas was evolved (about two hours) after which no more nitrogen was obtained. The solvents were evaporated in a stream of air, and the residue taken up with ether. The ethereal solution was then dried and fractionated. A yield of 12.5 g. of methyl 3-furanacetate (b.p. 89.8° (21 mm.)) was obtained. The ester was saponified, the mixture acidified, and the acid recovered by ether extraction. After drying and evaporation of the ether, the 3-furanacetic acid was recrystallized from petroleum ether to give 10.5 g. (41% based on furoyl chloride) of glistening white plates, m.p. 61.5–62.1°. *Anal.* Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.13, 57.18; H, 4.79, 4.71.[11]

The neutral equivalents of the acids used are as follows: 2-furoic, 111.9 (calcd., 112.1); 2-furanacetic, 126.3 (calcd., 126.1); 3-furoic, 112.7 (calcd., 112.1); and 3-furanacetic, 126.0 (calcd., 126.1).

The dry methanol for esterification runs was prepared by careful fractionation of du Pont methanol through an eight-foot helix-packed column. Methanol–hydrogen chloride solutions were prepared as in previous work.[12] The method for obtaining rate constants was essentially the same as that previously reported. Corrections were made for solvent expansion as well as for the volume change caused by solution of the solid acid in the methanol. Titrations were made using carbonate-free sodium hydroxide and phenolphthalein indicator. The initial concentration of organic acid was 0.5 *M*, while that of HCl catalyst was 0.005 *M*.

The acetic acid used as a solvent in the hydrogenation runs was prepared by fractionation in a five-foot helix-packed still. The platinum catalyst was prepared by

---

[1] H. A. Smith and H. T. Meriwether, THIS JOURNAL, **71**, 413 (1949).

[2] H. A. Smith and J. Burn, *ibid.*, **66**, 1494 (1944).

[3] H. A. Smith, D. M. Alderman and F. W. Nadig, *ibid.*, **67**, 272 (1945).

[4] H. A. Smith and J. F. Fuzek, *ibid.*, **71**, 415 (1949).

[5] J. Plucker and E. D. Amstutz, *ibid.*, **62**, 1512 (1940).

[6] T. Reichstein, A. Grussner, K. Schindler and E. Hardmeier, *Helv. Chim. Acta*, **16**, 278 (1933).

[7] W. H. Kirkpatrick, "The Physiological Action of Some Furan Compounds," Ph.D. Thesis, Iowa State College, 1935, p. 18.

[8] Preliminary experiments using small quantities of tetracarboxylic acid showed that evolution of 2.4 moles of gas per mole of starting material gave the maximum yield of the desired product.

[9] H. Gilman and R. R. Burtner, THIS JOURNAL, **55**, 2906 (1933).

[10] M. S. Newman and P. F. Beal, *ibid.*, **72**, 5163 (1950).

[11] Analysis performed by Galbraith Microanalytical Laboratories.

[12] H. A. Smith, THIS JOURNAL, **61**, 254 (1939).

standard methods.[13] The hydrogenations were carried out in a standard low-pressure Parr catalytic reduction apparatus equipped with a modified tank and a special gage.

Cleavage Products

The amounts of hydrogen absorbed by the acids indicated the formation of cleavage products. Positive identification of each cleavage product was not obtained, but evidence given below points to the formation of the following materials in addition to the tetrahydrofuran-substituted acids: 2-furoic, $HOCH_2CH_2CH_2CH_2COOH$; 2-furanacetic, $CH_3CH_2CH_2CH(OH)CH_2COOH$; 3-furoic, $HOCH_2CH_2CH(CH_3)COOH$; and 3-furanacetic, $CH_3CH_2CH(CH_2OH)CH_2COOH$.

The hydrogen uptake for 3-furoic acid indicated the formation of cleaved product only. The two isomers which could be formed are α-methyl-γ-hydroxybutyric acid and α-hydroxymethylbutyric acid. Distillation of the hydrogenated product gave material which boiled at 199–201° and had a refractive index, $n^{20}D$, of 1.4307. The literature values for the lactone of α-methyl-γ-hydroxybutyric acid are: b.p. 200–201° (745 mm.), $n^{24}D$ 1.4282.[14]

The hydrogen uptake of 3-furanacetic acid also indicated the formation of cleaved products only. Here the possible cleavage products are β-hydroxymethylvaleric acid and β-methyl-δ-hydroxyvaleric acid. It seems probable that either of these would distil as a lactone. The boiling point of β-hydroxymethylvalerolactone is reported as 99° (12 mm.) while that of β-methyl-δ-hydroxyvalerolactone is reported to be 90° (12 mm.).[15] Since the major portion of the hydrogenated product distilled at 98.9–99.7° (12 mm.), it appears that β-hydroxymethylvaleric acid is the chief cleavage product. The hydrogen uptake of 2-furanacetic acid indicated about 50% cleavage. The two possible cleavage products are β-hydroxycaproic acid and ε-hydroxycaproic acid. The only evidence indicating which of these two is formed was obtained when the hydrogenation product was esterified and subsequently distilled. A small fraction of material was found which decolorized a bromine solution, indicating unsaturation. Since β-hydroxy acids dehydrate much more readily than ε-hydroxy-acids, this was taken as an indication that the cleavage product contained β-hydroxycaproic acid.

The cleavage products for the hydrogenation of 2-furoic acid have been previously investigated.[4]

Experimental Calculations and Results

The rate constants for the acid-catalyzed esterification of the furoic and furanacetic acids were calculated from Goldschmidt's equation[16]

$$k = \frac{(r + a) \ln a/(a - x) - x}{(\text{catalyst}) rt}$$

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst for the experiments reported here is hydrogen chloride. The constant r allows for the fact that the real reaction is between the organic acid and the complex ROH_2^+, and the concentration of the latter is affected by the presence of water formed as a product of the reaction. The water reacts with the conjugate acid of the alcohol according to the equation

$$ROH_2^+ + H_2O \rightleftarrows ROH + H_3O^+$$

and r is defined by the expression

$$r = (ROH_2^+)(H_2O)/(H_3O^+)$$

The values of r used for methanol–water systems at 25, 35, 45 and 55° were 0.22, 0.28, 0.36 and 0.48.

Since the reaction of methanol and the HCl catalyst was appreciable during the esterification runs involving the furoic acids at the higher temperatures, it was necessary to correct the concentration of catalyst accordingly. Corrections were made in the same manner as previously described.[17]

The results for a typical run are shown in Table I, while the rate constants and activation energies for all of the esterification reactions are given in Table II. The activation energies were obtained from the Arrhenius equation using the method of least squares. A plot of log k against the reciprocal of absolute temperature is shown in Fig. 1.

TABLE I

ESTERIFICATION OF 3-FUROIC ACID AT 35°

t, min.	$(a - x)$	(HCl)	k (liters moles^{-1} sec.$^{-1}$)
2009	0.4018	0.00496	0.000430
3229	.3656	.00493	.000412
5413	.3114	.00489	.000407
7638	.2710	.00484	.000400
10332	.2296	.00479	.000405
13220	.1993	.00472	.000398
		Average	.000409

TABLE II

RATE CONSTANTS FOR THE ESTERIFICATION OF THE FUROIC AND FURANACETIC ACIDS

Acid	$k \times 10^4$ (liters moles^{-1} sec.$^{-1}$) 25°	35°	45°	55°
2-Furoic	0.828	2.03	4.62	9.88
E = 16,100	0.821	2.05	4.72	9.83
Av.	0.825	2.04	4.67	9.86
2-Furanacetic	259	464	801	1240
E = 10,200	262	465	776	1260
Av.	261	465	789	1250
3-Furoic	1.93	4.13	9.47	19.2
E = 15,200	1.95	4.09	9.18	18.4
Av.	1.94	4.11	9.33	18.8
3-Furanacetic	451	757	1196	1884
E = 9100	446	757	1232	1848
Av.	449	757	1214	1866

It has already been shown that the hydrogenation of the furan ring over platinum in acetic acid solution is first order with respect to hydrogen pressure, zero order with respect to the concentra-

---

[13] R. Adams, V. Voorhees and R. L. Shriner, *Org. Syntheses*, **8**, 92 (1928).

[14] R. Adams and E. F. Rogers, THIS JOURNAL, **63**, 234 (1941).

[15] S. S. G. Sircar, *J. Chem. Soc.*, 901 (1928).

[16] See especially H. Goldschmidt and O. Udby, *Z. physik. Chem.*, **60**, 728 (1907); H. Goldschmidt and A. Theusen, *ibid.*, **81**, 30 (1912); H. Goldschmidt and R. S. Melbye, *ibid.*, **143**, 139 (1929); Goldschmidt, Haaland and Melbye, *ibid.*, **143**, 278 (1929). The derivation of Goldschmidt's equation has been summarized by Smith, ref. 12.

[17] H. A. Smith, THIS JOURNAL, **62**, 1136 (1940).

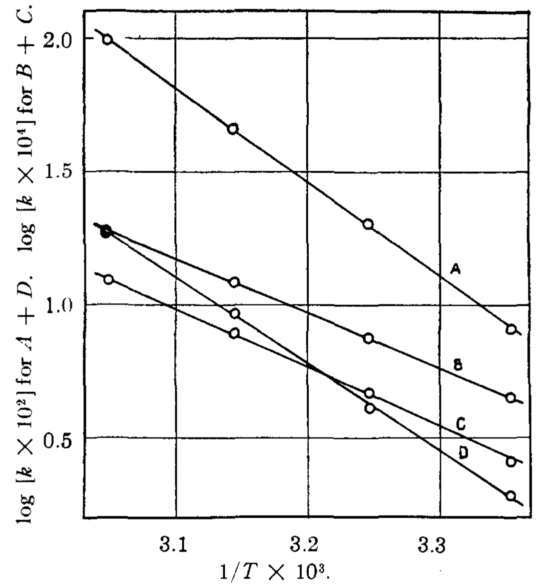


Fig. 1.—Temperature coefficients for esterification of furoic and furanacetic acids: A, 2-furoic; B, 3-furanacetic; C, 2-furanacetic; D, 3-furoic.

tion of hydrogen acceptor, and directly proportional to the weight of catalyst used provided shaking equilibrium is maintained.[4] This kinetic behavior was verified for the hydrogenation of the furoic and furanacetic acids. The values of the first order rate constants for these reactions were determined from the slopes of the lines obtained by plotting the logarithm of the pressure against time. Such constants were determined at several temperatures, and their logarithms plotted against the reciprocals of the absolute temperatures at which they were determined. Figure 2 shows the results. The values of the rate constants (referred to one gram of standard platinum catalyst and one liter hydrogen volume[4]) together with the activation energies for the hydrogenation reactions are given in Table III.

TABLE III

RATE CONSTANTS FOR THE HYDROGENATION OF THE FUROIC AND FURANACETIC ACIDS

Acid	$k_{1.0} \times 10^4$ (liters/g. min.)					
	16°	20°		30°		40°
2-Furoic	846	1077		1635		2540
$E = 8100$[a]				1643		
				1453		
				1961		
	20°	30°		40°		50°
2-Furanacetic	2010	3360		5750		8650
$E = 9100$	2280	3420		6110		
	20°	30°		40°		50°
3-Furoic	1895	2530		4500		4860
$E = 7600$		2480				
		2620				
		2480				
	20°	25°	30°	35°	40°	45°
3-Furanacetic	2400	3215	3800	4630	5435	7420
$E = 8000$						

[a] A previously reported figure was apparently in error due to catalyst poisoning. The present revised value is more in line with that found for similar compounds. See H. A. Smith and J. F. Fuzek, reference 4.

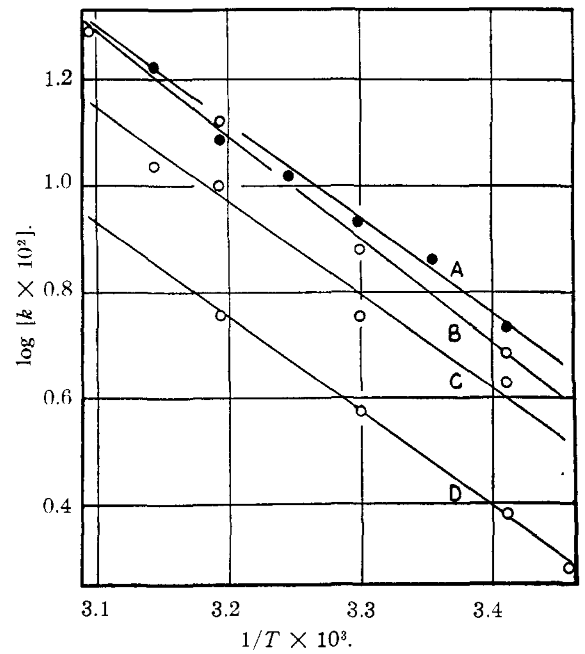
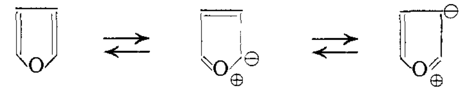


Fig. 2.—Temperature coefficients for hydrogenation of furoic and furanacetic acids: A, 3-furanacetic; B, 2-furanacetic; C, 3-furoic; D, 2-furoic. (Note: All values of k should be multiplied by 4.43 to yield the values in Table IV.)

Discussion

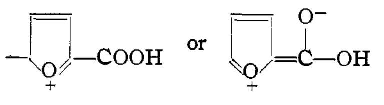
An examination of Table II shows the influence of resonance between the furan nucleus and carboxyl group. In the unconjugated furanacetic acids, the rate constants and activation energies for esterification are approximately those expected for a substituted acetic acid. (For esterification of cyclohexanecarboxylic acid, $k_{25} = 0.0118$, $E = 10{,}000$ calories per mole.[18]) However, for the furoic acids, where the carboxyl and furan groups are conjugated, the rate is less than one per cent. of that for the non-conjugated acids, and the activation energy is increased by 5000–6000 calories per mole. The results are very similar to those for benzoic acid ($k_{25} = 0.000217$, $E = 14{,}600$).[19]

It is interesting to note that for both furoic and furanacetic acids, the 2-acids react about one-half as fast as do the 3-acids. The resonance of the furan ring may be represented as



I II III

The charge-separated isomer II is much more important than III. The esterification results may indicate that resonance within the hybrids

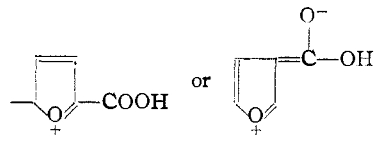


found in the 2-acid is greater than within the corresponding forms

---

(18) H. A. Smith and H. S. Levenson, THIS JOURNAL, **62**, 2733 (1940).

(19) H. A. Smith and R. B. Hurley, *ibid.*, **72**, 112 (1950).



found in the 3-acid. On the other hand, the fact that the furanacetic acids also show similar differences may indicate that the inductive effect of the furan ring when substituted in the 2-position is greater than when substituted in the 3-position.

An examination of Table III shows that there is little influence of conjugation on the rate of hydrogenation over platinum catalyst. All four acids have the same rate constants within a factor of approximately two, while the activation energies are essentially within the experimental error. (It is estimated that the error in activation energies for the esterification reactions is ±200 calories, while for the hydrogenations the error is of the order of ±500 calories.) This indicates that the resonance between the groups is destroyed when the acids are adsorbed by the platinum. This is probably caused by destruction of the resonance of the furan ring itself, since the carboxyl group is presumably not influenced by the course of the reaction.

Acknowledgment.—The authors are indebted to the Office of Naval Research for financial support which made this research possible.

KNOXVILLE, TENNESSEE RECEIVED APRIL 6, 1951

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Rate of Rise of Liquids in Fine Vertical Capillaries

BY JOSEPH R. LIGENZA[1] AND RICHARD B. BERNSTEIN

The rates of ascent of several liquids in two vertical fine capillary tubes have been measured. By the use of tubes of radii 0.002 to 0.005 cm., in which the rate of rise is quite slow for most liquids, precise data are readily obtained. The small velocity makes possible a simplification of the differential equation of motion, resulting in a simple solution suitable for direct comparison with experiment. The data could be represented by this expression over the entire ascent. For the initial portion of the rise in short, fine vertically mounted capillaries, the equation reduces to the approximation $h^2 = R\gamma t/4\eta$, suggesting a rapid and simple method for the estimation of the viscosity of micro quantities of liquids.

Introduction

Although considerable theoretical work on the problem of the rate of capillary rise has been carried out, few precise experimental data are available to allow critical evaluation of the theoretical results.[2-7] Those data in the literature were obtained for only a few liquids, using rather large bore capillaries, of radii 0.01 to 0.04 cm. With tubes of this size the initial rate of rise is very rapid, requiring special techniques for the measurements, which were not of high precision. This paper is concerned with the rise of various liquids in fine capillaries, of radii 0.002 to 0.005 cm. The use of fine tubes has the advantage that the heights travelled by the liquid are much greater, and that the rate of ascent is slow enough for precision measurement. In addition, the slow rate of rise makes possible an appreciable simplification of the differential equation of motion, without sacrifice of rigor. The solution is in a form suitable for direct comparison with experiment.

An exact treatment of the rise of a liquid in a vertical capillary under the influence of its surface tension would be very difficult. Neither the hydrodynamic problem of accelerated flow nor the physico-chemical problem of the rate of wetting is well understood. With the usual assumptions that Poiseuille's law obtains for the non-stationary state, and that wetting is very rapid, the differential equation of motion is

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\pi R^2[\rho h + \rho_a(l - h)]\frac{\mathrm{d}h}{\mathrm{d}t}\right\} = 2\pi R\gamma \cos\theta - 8\pi\frac{\mathrm{d}h}{\mathrm{d}t}[\eta h + \eta_a(l - h)] - \pi R^2 gh(\rho - \rho_a) - \frac{1}{4}\pi R^2\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}\right)^2 \quad (1)$$

where h is the height of the column of liquid at time t, R and l are the radius and length of the capillary, η and η_a the viscosity of the liquid and of air, respectively, ρ and ρ_a the density of liquid and air, while γ is the surface tension (liquid–air) and θ the contact angle, assumed constant. The term on the left is the rate of change of the momentum of the contents of the capillary; the terms on the right are, respectively, forces due to surface tension, viscous resistance, gravity, and the "end-drag effect" of Brittin.[5b]

Equation 1 is not amenable to explicit solution. However, for a tube of *sufficiently small* radius, the rate of rise may be slow enough so that the rate of change of momentum and end-drag terms are negligible with respect to the others. The solution for this simplified case of Equation 1 is then

$$t = \frac{8}{R^2\rho g}\left\{[(\eta - \eta_a)h_\infty + \eta_a l]\ln\left(\frac{h_\infty}{h_\infty - h}\right) - (\eta - \eta_a)h\right\} \quad (2)$$

where $h_\infty = 2\gamma\cos\theta/R\rho g$.

For convenience, the final height, h_∞, (an experimentally measurable quantity), has been introduced into the equation; also, $(\rho - \rho_a)$ has been approximated by ρ.

Equation 2 is equivalent to the result of Washburn,[3] reduced to zero hydrostatic head. How-

---

[1] Department of Chemistry, Columbia University, New York, N. Y.

[2] E. J. LeGrand and W. A. Rense, *J. Appl. Phys.*, **15**, 456 (1944).

[3] E. W. Washburn, *Phys. Rev.*, **17**, 273 (1921).

[4] C. H. Bosanquet, *Phil. Mag.*, **6**, 525 (1923).

[5] (a) G. Pickett, *J. Appl. Phys.*, **15**, 623 (1944); (b) W. E. Brittin, *ibid.*, **17**, 37 (1946).

[6] J. M. Bell and F. K. Cameron, *J. Phys. Chem.*, **10**, 658 (1906).

[7] R. L. Peek and D. A. McLean, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 85 (1934).