

The Kinetics of the Acid-Catalysed Hydrolysis of Alkyl Formates

PENTTI SALOMAA

Department of Chemistry, University of Turku, Turku, Finland

The acid-catalysed hydrolysis of ethyl, *sec.*-propyl and *tert.*-butyl formates has been studied kinetically in aqueous solutions over a wide range of temperature (15°C–86°C). The rate coefficients for ethyl and *sec.*-propyl formates are in reasonable accord with the Arrhenius equation over the whole temperature range, but the plot of $\log k$ against reciprocal absolute temperature for *tert.*-butyl formate is linear only in the low temperature range. The results suggest that all three esters are hydrolysed by essentially the same mechanism, a bimolecular acyl-oxygen fission, at the low temperatures. In the case of *tert.*-butyl formate, however, another mechanism which has a higher activation energy and which presumably involves unimolecular alkyl-oxygen fission, significantly augments the rate at the higher temperatures.

The hydrolysis reactions of the same esters have also been studied at 25°C in the presence of hydrogen chloride concentrations up to 3 M. The influence of the catalyst concentration on the rate was found to be similar for all the esters, and furthermore closely resembled its influence on the rate of hydrolysis of ethyl acetate. This is also in accord with the view that the hydrolysis of the three esters takes place by an essentially similar mechanism under these conditions.

It is well known that the acid-catalysed hydrolysis reactions of formic esters proceed at appreciably higher rates than the acid-catalysed hydrolysis reactions of the corresponding acetic esters in which a bimolecular acyl-oxygen fission is assumed to take place¹. For this reason a change to a unimolecular alkyl-oxygen fission mechanism, which becomes apparent in different ways with the acetic esters^{1,2} when the alkyl groups of the esters are varied in the sequence ethyl, *sec.*-propyl and *tert.*-butyl, may be expected to be less pronounced with the formic esters. Stimson³, for example, concluded from the values of the Arrhenius parameters for the hydrolysis of *tert.*-butyl formate in acetone-water solution (60 % acetone by volume) that the mechanism of the reaction represents a bimolecular acyl-oxygen fission. So far as the hydrolysis in aqueous acid solutions is concerned, where the proton availability is much greater than in acetone-water mixtures⁴ and which may therefore

be expected to favour the unimolecular mechanism, data for *tert.*-butyl formate have not been reported. The results of a kinetic study of the hydrolysis of alkyl formates in aqueous hydrogen chloride solutions, which is an extension of an earlier study of the acid hydrolysis of aliphatic esters ^{2,5}, are presented and discussed in the following.

EXPERIMENTAL

Materials. Ethyl and *sec.*-propyl formates were prepared by customary methods ⁶ and purified by efficient fractional distillation. *tert.*-Butyl formate was synthesized by a method described recently by Young and Paré ⁷, in which *isobutylene* is passed into anhydrous formic acid to which cation exchange resin (Dowex X 50) has been added. The *isobutylene* was prepared by adding *tert.*-butyl alcohol dropwise to a large excess of anhydrous oxalic acid at a temperature of 80–90°C. The physical constants of the *tert.*-butyl formate after it had been fractionally distilled (*b. p.* 82.8°C at 755 mm Hg, d_{25}^{25} 0.8694, n_D^{25} 1.3787) were in accord with those reported by Young and Paré. The purities of the esters were checked by hydrolysing known weights in dilute acid solution and determining the formic acid produced by alkalimetric titration. The consumption of base did not deviate by more than 2 % from the calculated amount.

Kinetic measurements. Depending on the conditions, three different methods were employed in following the progress of the reactions. The first method, which was used to follow the reactions at 25°C when the catalyst acid concentration was high compared to that of the ester, has previously been described by the writer ^{5,2} and is based on the determination of the concentration of unreacted ester in samples removed from the reaction mixture after suitable intervals. The second method, which was used when the catalyst concentration and reaction temperature were relatively low (see below), was based on the alkalimetric titration of the formic acid present in samples pipetted from the reaction mixture. In the third method, employed at temperatures where volatility was appreciable, aliquots of the reaction mixture were transferred to ampoules which were sealed by fusion to avoid volatilization and which were opened after suitable intervals for the titrimetric determination of the liberated formic acid. For temperatures of 45°C and higher, electrically heated oil thermostats regulated by mercury contact thermometers were employed, whereas at the lower temperatures similarly heated and regulated water thermostats were used. The temperatures of the thermostats remained constant within $\pm 0.03^\circ\text{C}$.

The time periods used when the first method was employed to analyse the unreacted ester by alkaline hydrolysis were much shorter for the formic esters than for acetic esters ² because of the higher rates of alkaline hydrolysis of the former esters. Periods of only a few minutes were considered sufficient in the case of ethyl and *sec.*-propyl formates. With *tert.*-butyl formate, the rate of alkaline hydrolysis of which was unknown, a time of one hour was chosen and was found by separate experiments to be sufficiently long. In the above experiments, as well as in those described below, the initial ester concentration was between 0.1 and 0.16 M.

In the second method, 5 ml samples taken with a semiautomatic pipette from the reaction mixtures were run into ice-water mixtures to arrest the reaction and titrated immediately in a nitrogen atmosphere (to exclude carbon dioxide) with 0.07–0.11 N standard sodium hydroxide to the phenolphthalein endpoint. Because each sample was cooled and diluted and the titration performed rapidly, no appreciable hydrolysis of the ester took place. Zero time was chosen as the time of taking the first sample. From 8 to 10 samples were withdrawn during the reaction in addition to those taken to determine the final value.

In the third method, the reaction mixture was prepared by mixing the components at 25°C, after which twelve 5 ml aliquots were pipetted into 6–7 ml glass ampoules. After the ampoules had been sealed by fusion, they were transferred simultaneously to a thermostat, the temperature of which was usually much above 25°C. After the ampoules had warmed to the temperature in the thermostat (in separate experiments a period of 5–10 min was found sufficient for the temperatures to become uniform in the solutions when

the group of ampoules was vigorously shaken), two ampoules were removed and cooled rapidly by shaking them in ice-water. After the ampoules had been opened, the acid in the solutions was titrated as in the second method. The time when the two ampoules were immersed in the ice-water mixture was taken as zero time and the mean base consumption as the initial value in the calculation of rate coefficients. Seven further samples were taken at intervals during the course of the reaction and titrated. The total amount of acid present at the end of the reaction was determined by titrating the samples in the three remaining ampoules after a sufficiently long period of time; the mean base consumption for these samples was employed as the final value. The procedure in which initial samples are analysed under the same conditions as the other samples taken during the course of the reaction reduces the time error to a minimum and is easily applied in practice. In principle it is of no importance how far the reaction has progressed before the first sample is taken.

Since in the experiments described the concentrations were measured at 25°C, usually a much lower temperature than that at which the reaction took place, the actual concentrations were calculated using the values of the density of water at different temperatures given in the International Critical Tables⁶.

The change from the second to the third method of following the reaction took place with *sec.*-propyl and *tert.*-butyl formates at 45°C and 55°C, respectively, but with ethyl formate, owing to its greater volatility, at 25–35°C. The second and third methods were compared using ethyl formate at 25°C; the value of the second-order rate coefficient was 0.00337 l mole⁻¹ s⁻¹ when the second method was employed and 0.00335 l mole⁻¹ s⁻¹ when the third method was employed.

Kinetic equations for low catalyst concentrations. When relatively high catalyst acid concentrations were employed, the hydrogen ion concentration in the reaction mixture remained practically constant as the reaction progressed and the first-order rate law was satisfactorily obeyed. However, as it was necessary to employ relatively low catalyst acid concentrations at the highest temperatures because of the high reaction rates, the formic acid produced catalysed the reaction and this had to be taken into account in the calculations. In extreme cases, the increase in the hydrogen ion concentration during the reaction represented the greater part of the total catalyst concentration at the end of the reaction.

The time law for the reaction is

$$\frac{dx}{dt} = k_c C_{\text{H}^+} (a-x) \quad (1)$$

where a denotes the ester concentration at zero time, x the decrease in this concentration during time t , k_c the second-order rate coefficient and C_{H^+} the hydron concentration, which was also a function of time in the experiments. Since $x = 0$ when $t = 0$, eqn. (1) yields on integration

$$k_c = \frac{\ln [a/(a-x)]}{\int_0^t C_{\text{H}^+} dt} = \frac{(1/t) \ln [a/(a-x)]}{(1/t) \int_0^t C_{\text{H}^+} dt} = \frac{k_t}{(C_{\text{H}^+})_t} \quad (2)$$

where k_t is the value of the rate coefficient computed from the usual first-order rate equation. This first-order coefficient has different values at different times during the course of the reaction and the corresponding hydron concentration

$$(C_{\text{H}^+})_t = \frac{1}{t} \int_0^t C_{\text{H}^+} dt \quad (3)$$

is the time average of the hydron concentration over the interval $(0, t)$. The value of the integral in eqn. (3) can be determined when the variation of the hydron concentration with time is known. The integral was calculated as a sum of trapezoids by a method described by the writer in connection with a study of the alcoholysis of α -halogenoethers⁹. The hydron concentration at each time of sampling was determined as follows. The initial concentration of hydrogen chloride in the reaction mixture in moles per litre

Table 1. The hydrolysis of *sec.*-propyl formate at 86.22°C. ml NaOH = ml of 0.1102 N sodium hydroxide solution consumed in the titration of the sample. Sample volume (measured at 25°C) 5.01 ml. The coefficient for the thermal expansion from 25°C to 86.22°C is 1.0301. $10^3 K = 0.1206$ mole l⁻¹, $10^3 c = 0.816$ mole l⁻¹ (at 86.22°C).

<i>t</i> min.	ml NaOH	$10^3 k_t$	$10^3 f$	$10^3 C_{H^+}$	$10^3 (C_{H^+})_t$	$10^3 k_c$
0	0.57	—	11.3	1.605	—	—
4	1.30	395	26.9	2.209	1.907	207
10	2.68	505	56.4	2.997	2.325	217
15	3.76	559	79.5	3.479	2.629	213
20	4.65	587	98.5	3.826	2.885	203
25	5.64	660	119.6	4.174	3.108	212
30	6.43	720	136.5	4.432	3.307	218
42	7.48	770	158.9	4.750	3.674	210
∞	8.64	—	—	—	—	—

$$\text{Average } k_c = 0.211 \text{ l mole}^{-1} \text{ s}^{-1}$$

(denoted by *c*) was determined when the reaction medium was prepared. The total acid concentration in the sample is given by (*c* + *f*), where *f* is the concentration of the formic acid formed. The hydron concentration in the reaction mixture at the time of sampling can be computed from

$$C_{H^+} = \frac{1}{2}(c-K) + \sqrt{\frac{1}{4}(c-K)^2 + (c+f)K} \quad (4)$$

where *K* is the acid dissociation constant of formic acid at the temperature in question. For the temperature dependence of this dissociation constant, Harned and Embree¹⁰ have given the following equation

$$\log K = - (173.624/T) + 17.88348 \log T - 0.0280397 T - 39.06123 \quad (5)$$

Although this equation is based on experimental data for the temperature range from 0° to 60°C, the general thermodynamic form of the equation and the fact that the value of *K* varies only slightly with temperature justified the use of the equation for extrapolation to obtain the values of the constant at temperatures above 60°C. Furthermore, any error resulting from the use of the equation was the same for all the esters studied and hence the values of the rate coefficients for the latter are comparable at each temperature. In addition, the fact that the data for ethyl and *sec.*-propyl formates obeyed the Arrhenius equation with satisfactory accuracy over the temperature range where eqn. (5) was employed showed that no serious errors resulted. As far as the effect of electrolyte concentration on the values of *K* is concerned, this could be disregarded because the ionic strength was very low in the experiments in which eqns. (2), (3), (4) and (5) were applied.

The data in Table 1 refer to a case where the initial concentration of hydrogen chloride was lower than the hydron concentration due to the dissociation of formic acid produced in the reaction. The large increase in the values of *k_t* as the reaction progressed shows that the reaction was autocatalytic. On the other hand, the calculated values of *k_c* at different stages of the reaction are essentially constant, which shows that the equations employed correctly represent the course of the reaction. It may be mentioned, however, that constant values would have been obtained for *k_c* even if values of *K* deviating slightly from those derived from eqn. (5) had been employed. This is due to the fact that in this extreme case the second term under the root sign in eqn. (4) primarily determines the value of the hydron concentration. Therefore the value of *k_c* includes, in addition to the usual experimental errors in kinetic measurements, the error in the value of *K*.

Table 2. The rate coefficients of the acid-catalysed hydrolysis of alkyl formates at different temperatures and the values of the parameters of the Arrhenius equation computed from the data for the lower temperatures (15–45.5°C).

°C	$10^3 k_c$ in $l \text{ mole}^{-1} \text{ s}^{-1}$		
	Ethyl formate	<i>sec.</i> -Propyl formate	<i>tert.</i> -Butyl formate
15.00	1.33	1.18	2.62
25.00	3.36	2.92	5.98
35.00	7.58	6.85	13.0
45.48	17.4	15.6	31.4
55.63			60.5
66.06			117.4
68.48	98.0		
76.15			314
86.22	294	211	683
15.00– 45.48	$E = 15\,340$ cal per mole, $\log A = 8.76$	$E = 15\,440$ cal per mole, $\log A = 8.79$	$E = 14\,790$ cal per mole, $\log A = 8.62$

RESULTS AND DISCUSSION

The acid-catalysed hydrolysis of alkyl formates could be followed kinetically by the methods described above over the temperature range from 15 to 86°C. The results of the experiments are collected in Table 2. Rate coefficients of the acid-catalysed hydrolysis of ethyl and *sec.*-propyl formates at relatively low temperatures have been reported previously. For comparison, the following values in $l \text{ mole}^{-1} \text{ s}^{-1}$ units referring to 25°C may be mentioned: ethyl formate, 0.00312 (Palomaa¹¹), 0.00325 (Salmi¹²), 0.00307 (Tommila and Hella¹³); *sec.*-propyl formate, 0.00280 (Palomaa¹¹), 0.00293 (Palomaa *et al.*¹⁴).

The plots of the logarithm of the rate coefficient against reciprocal absolute temperature in Fig. 1 show that the Arrhenius equation is obeyed well by the data for the three formic esters at relatively low temperatures. The values of the activation energy and frequency factor computed by the method of least squares from the data referring to the temperature range from 15 to 45.5°C are given in Table 2; in this temperature range the plots are satisfactorily linear for all three esters. Since the values of the activation energy and the frequency factor for *tert.*-butyl formate are of the same magnitude as the values for ethyl and *sec.*-propyl formate in this temperature range, there is no reason to believe that the mechanism of hydrolysis of the first-mentioned ester differs essentially from that of the last two esters, *i.e.* all three esters presumably hydrolyse under the conditions by the normal mechanism of acid-catalysed ester hydrolysis designated as $A_{AC}2$ by Ingold¹.

It will be seen from Fig. 1 that the behaviour of *tert.*-butyl formate deviates from that of the other two esters at higher temperatures in that its rate coefficient increases more rapidly with temperature than the Arrhenius parameters

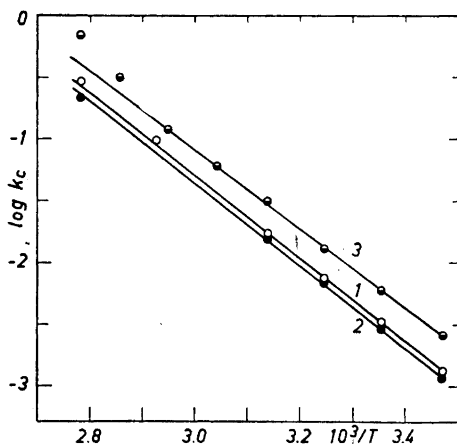


Fig. 1. Plots of $\log k_c$ against $1/T$ for the hydrolysis reactions of alkyl formates in dilute acid solution. 1. Ethyl formate. 2. *sec.*-Propyl formate. 3. *tert.*-Butyl formate. The straight lines are Arrhenius plots based on data obtained in the temperature range 15–45.5°C.

computed from the data for lower temperatures would imply. This different behaviour cannot be attributed to systematic errors in the method of following the reaction at the higher temperatures because the data obtained for ethyl and *sec.*-propyl formates by the same experimental procedure exhibit only slight deviations from the linear dependence of $\log k_c$ on reciprocal temperature.

The different behaviour of *tert.*-butyl formate at the higher temperatures suggests that under these conditions, in addition to the $A_{AC}2$ mechanism, another hydrolysis mechanism with a higher activation energy begins to contribute to the rate. This assumption is supported by the following rough estimates. If we assume that the Arrhenius equation based on the data obtained at the lower temperatures relates to the $A_{AC}2$ mechanism and also applies as far as this mechanism is concerned at the higher temperatures, as it approximately does in the case of ethyl and *sec.*-propyl formates, it is possible to determine the contribution of the $A_{AC}2$ mechanism to the rate of hydrolysis of *tert.*-butyl formate at the higher temperatures. When the rate coefficients of hydrolysis by the $A_{AC}2$ mechanism calculated for the higher temperatures are subtracted from the over-all observed rate coefficients, the resulting rate coefficients should represent the contribution of the assumed concurrent mechanism. The latter rate coefficients calculated from the data for *tert.*-butyl formate given in Table 2 are $0.261 \text{ l mole}^{-1}\text{s}^{-1}$ at 86.22°C and $0.082 \text{ l mole}^{-1}\text{s}^{-1}$ at 76.15°C. The values of the parameters of the Arrhenius equation derived from these rate coefficients are $E = 29 \text{ kcal per mole}$ and $\log A = 17$ and are of such magnitudes that they can be taken to refer to the unimolecular alkyl-oxygen fission mechanism of acid-catalysed ester hydrolysis ($A_{AL}1$). For the acid-catalysed hydrolysis of *tert.*-butyl acetate, for example, which hydrolyses primarily by the unimolecular $A_{AL}1$ mechanism^{1,2}, the values of the parameters computed from the data reported by Palomaa *et al.*¹⁴ are $E = 27.6 \text{ kcal per mole}$ and $\log A = 16.34$. From the values derived for the Arrhenius parameters one can estimate the rate coefficient of the hydrolysis of *tert.*-butyl

formate by the A_{AL1} mechanism to be about 10^{-4} l mole $^{-1}$ s $^{-1}$ at 25°C and hence this mechanism contributes very little to the over-all rate of hydrolysis, 59.8×10^{-4} l mole $^{-1}$ s $^{-1}$, at this temperature.

It will be noted that the rates of hydrolysis by the A_{AL1} mechanism of acetic esters do not differ greatly from the rates of hydrolysis of the corresponding formic esters, whereas in the case of the A_{AC2} mechanism a corresponding change in structure leads to a marked change in reactivity. In water and water-alcohol mixtures, alkoxymethyl formates react by the A_{AL1} mechanism only from 1.5 to 3 times as fast as the corresponding acetates¹⁵. If the rate coefficient for the hydrolysis of *tert.*-butyl acetate² in dilute acid at 25°C, 1.34×10^{-4} l mole $^{-1}$ s $^{-1}$, can be taken to represent hydrolysis by the unimolecular A_{AL1} mechanism, the magnitude of the estimated rate coefficient of the hydrolysis of *tert.*-butyl formate by the same mechanism at 25°C, 10^{-4} l mole $^{-1}$ s $^{-1}$, is plausible.

One particular point of interest concerning the effect of structure on hydrolysis by the bimolecular A_{AC2} mechanism is that when the alkyl group changes from ethyl to *tert.*-butyl the rate becomes smaller in the case of acetates in such a degree that the unimolecular A_{AL1} mechanism begins to predominate, whereas in the case of formates the rate increases (*e.g.*, about twofold at 15°C). This latter increase in rate is not, at least not at the lower temperatures, due to a change in mechanism from A_{AC2} to A_{AL1} , as other experimental evidence would lead one to conclude. This different effect of alkyl group structure in the hydrolysis of formates and acetates by the A_{AC2} mechanism is probably due to the combined effect of several factors. One possible explanation is that the retardation of the rate of hydrolysis when a tertiary alkyl group replaces a primary alkyl group in acetic esters is primarily due to steric hindrance, and the A_{AL1} mechanism, which is insensitive to steric effects, begins to predominate. In the case of the formic esters, steric hindrance is of lesser significance because in these compounds the carbonyl group is more exposed to the attack of a water molecule, and therefore the polar factors become more apparent. These assumptions are supported by the observation that at the lower temperatures where the different formic esters may be expected to react by the same mechanism the effect of structure on the rate becomes apparent primarily as a change in the activation energy

Table 3. The first-order rate coefficients k (in s $^{-1}$) for the hydrolysis of ethyl, *sec.*-propyl and *tert.*-butyl formates in aqueous hydrochloric acid solutions of various concentrations. Hydrochloric acid concentrations in moles per litre. 25°C.

Ethyl formate		<i>sec.</i> -Propyl formate		<i>tert.</i> -Butyl formate	
c_{HCl}	$10^3 k$	c_{HCl}	$10^3 k$	c_{HCl}	$10^3 k$
0.1512	0.503	0.1512	0.442	0.0841	0.503
0.349	1.21	0.748	3.02	0.497	3.47
1.35	6.00	1.35	6.08	1.36	11.2
2.09	9.90	2.09	10.4	2.10	21.0
2.96	13.5	2.96	14.3	2.97	33.8

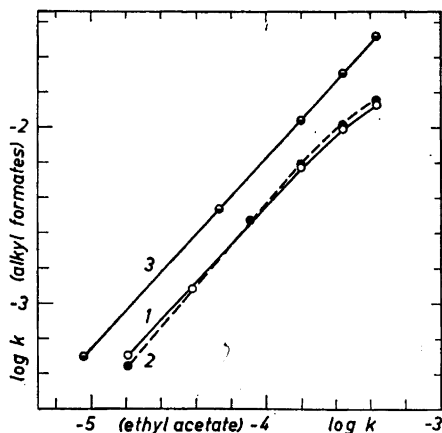


Fig. 2. Plots of the values of $\log k$ for alkyl formates against the values of $\log k$ for ethyl acetate at identical acid concentrations in aqueous hydrochloric acid solutions at 25°C. 1. Ethyl formate. 2. *sec.*-Propyl formate. 3. *tert.*-Butyl formate.

(see Table 2). The frequency factor, and hence the entropy of activation, does not vary significantly in value from one ester to the other, which suggests only slight changes in steric hindrance. A more detailed study of the effects of polar and steric factors on the acid-catalysed hydrolysis reactions of formic and acetic esters would be desirable.

Since the formic esters studied may be assumed to hydrolyse in acid solution at low temperatures by the bimolecular mechanism in which the critical complex includes a water molecule in addition to the ester molecule and a proton, these esters offered a possibility of studying the validity of the Zucker-Hammett hypothesis^{16,17} by carrying out kinetic measurements of the rates of hydrolysis in moderately acid solutions by the method previously described by the author^{5,2}. Measured values of the first-order rate coefficients, k , of the hydrolysis of the three formic esters in aqueous hydrochloric acid solutions of varying concentration are shown in Table 3. The data reveal that the rates for all three esters react similarly to a change in the medium and the values of k increase slightly more rapidly than they would if they were proportional to the molar concentration of the catalyst hydrochloric acid. The curves in Fig. 2, in which the values of $\log k$ for the formic esters are plotted against the values of $\log k$ for ethyl acetate for the same hydrogen chloride concentrations (the latter values interpolated from previously reported data^{5,2}), show that the effect of the acid medium on the rate is approximately the same for the formic esters as for ethyl acetate. The increase in the rate at the higher acid concentrations is, however, possibly slightly less rapid with the formic esters than with ethyl acetate. Since the rate of hydrolysis of ethyl acetate, in contrast to *tert.*-butyl acetate², follows more closely the acid concentration than the acidity function H_0 , in qualitative agreement with the expectations based on the Zucker-Hammett hypothesis, it follows from the plots in Fig. 2 and the discussion above that this hypothesis is approximately valid also for the formic esters in the investigated media.

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