NEW KINETIC METHODS. 2.* AN INDIRECT MEASUREMENT OF ESTER FORMATION AND HYDROLYSIS RATES

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The use of an assistant reagent to monitor spectroscopically the concentration of compounds that lack chromophores is described. It is demonstrated, for example, that the concentration of an aliphatic alcohol (present during acid-catalyzed hydrolysis or esterification reactions) can be monitored continuously by addition of a small amount of chromium trioxide. From a knowledge of the rate law and the rate constants for chromic acid oxidations, $-d[CrO_3]/dt = k[\text{alcohol}][CrO_3]$, the concentration of alcohol can be determined at any time by monitoring the absorbance of chromic acid at 363 nm. The rate at which the concentration of the alcohol is changing can then be used to calculate rate constants for the corresponding esterification or hydrolysis reactions. Rate constants obtained in this way are compared with those previously obtained by use of direct methods, and the application of this approach to the study of kinetics under conditions not accessible by other methods is illustrated.

INTRODUCTION

The rates of chemical reactions in solution are usually determined by monitoring a physical property that changes progressively as the reaction proceeds. Some procedures are continuous, others non-continuous. Methods relying on spectroscopic changes can usually be made continuous, as can conductance measurements, dilatometry and refractive index changes. Other methods which require the removal of an aliquot and quenching of the reaction followed by a quantitative analysis for one of the products of reactants are non-continuous.

Because spectroscopic methods are both convenient and reliable, it has become common practice to use substrates that exhibit well defined spectral changes whenever possible. For example, p-nitrophenyl esters have often been used as model compounds for the study of hydrolysis rates because of the distinctive UV absorption spectrum of the p-nitrophenolate ion.[1] However, because many aliphatic compounds lack chromophores that absorb in the ultraviolet and visible region, their reactions cannot be monitored by electronic spectroscopy as easily as those for aromatic compounds.

In this paper, a spectroscopic method for following the reactions of compounds lacking chromophores is described. The method involves addition of small

amounts of an assistant reagent that undergoes a spectral change when it reacts with one of the reactants or products. If the rate constant for its reaction with one of the products or reactants has been predetermined, the concentration of that species at any given time can be obtained from an analysis of the rate at which the assistant reagent is reacting. An approach similar to this has previously been used non-continuously for monitoring ethanol concentrations by determining the rate at which aliquots reduce permanganate.[2] However, to the best of our knowledge, this is the first report of the use of an assistant reagent in a continuous fashion.

Consider as a concrete example the acidic hydrolysis of ethyl acetate:

$$CH_3CO_2CH_2CH_3 \xrightarrow{H^+/H_2O} CH_3CO_2H + CH_3CH_2OH$$

(1)
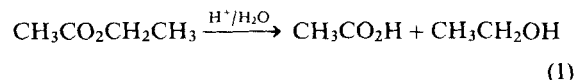
Although none of the compounds in equation (1) absorbs in a readily accessible region of the ultraviolet spectrum, the rate can be monitored by adding an assistant reagent, chromium trioxide, in amounts small compared with the concentration of ethyl acetate. Because CrO_3 does not react with either ethyl acetate or acetic acid under these conditions, its rate of reduction will be governed by the equation[3]

$$-d[CrO_3]/dt = k_2[CrO_3][CH_3CH_2OH]$$

(2)

Consequently, if it is possible to predetermine the rate constant, k_2, under these conditions and to

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*For Part 1 of this series, see Ref. 5.

monitor both $-d[CrO_3]/dt$ and $[CrO_3]$, the concentration of ethanol can be determined continuously. Because the changes that occur in the absorption spectrum of chromic acid when it is reduced are well defined,[4] the required rate information can be obtained by taking tangents to a plot of absorbance at 363 nm vs time.[5] The rate of hydrolysis can then be determined from the variation in ethanol concentration with time. The required calculations can, of course, be most easily accomplished by use of a computer and the appropriate numerical analysis software.

The results of such a study are reported in this paper. The rate constants obtained under certain conditions are compared with previously published values and the use of this method to study kinetics under conditions not accessible by other methods is illustrated.

EXPERIMENTAL

Materials. Esters, obtained commercially, were shaken with 3% sodium hydrogen carbonate to remove acids, washed with distilled water, dried over anhydrous calcium sulfate for 3 days and distilled through a 20 cm Vigreux column. Suitable fractions (Table 1) were collected for each compound. Gold label (+99%) alcohols, obtained from Aldrich, were also dried over anhydrous calcium sulfate for 3 days and then distilled through a Vigreux column. Suitable fractions (Table 1) were collected for each compound.[6]

Solutions of hydrochloric acid, sulfuric acid and perchloric acid were prepared by dilution of Fisher reagent-grade acids with doubly distilled water. Concentrations were determined by titration with standard-

ized sodium hydroxide solutions. Acetic acid was purified by distilling reagent-grade acid (Fisher) from 1% chromic acid through a Vigreux column.[7] The fraction boiling at 117–118 °C was collected and stored in an all-glass vessel.

Kinetic methods. Oxidation rate constants were predetermined by placing 2·00 ml of an aqueous acidic solution of the appropriate alcohol (*ca* 0·1 M) in a thermostated curvette. Concentrated aqueous CrO_3 (1·0 μl) was then added to produce a solution with an absorbance of about 0·9 (*ca* 5×10^{-4} M CrO_3) and the reduction of the oxidant was followed using a Hewlett-Packard Model 8485A spectrophotometer with a thermostated cell holder. The rates were obtained from plots of ln(absorbance – final absorbance) at 363 nm vs time (Figure 1).

Hydrolysis rates were determined by adding 0·2 mmol of ester to 2·00 ml of an aqueous acidic solution in a thermostated curvette. Concentrated aqueous chromic acid solution (1 μl) was added immediately and the rate of reaction monitored at 363 nm.

Esterification rates were determined by adding alcohol (10 μl) to 2·00 ml of aqueous acetic acid in a thermostated curvette, introducing 1 μl of concentrated CrO_3 solution and monitoring the rate as described above.

Calculation of hydrolysis rate constants, k_H. Because it is known that hydrolysis is a first-order reaction,[8] the concentration of ester at time t can be computed from the equation

$$[ester] = [ester]_0 e^{-k_H t} \qquad (3)$$

where $[ester]_0$ is the initial concentration of ester. The concentration of alcohol formed by hydrolysis of this ester would then be given by

$$[alcohol] = [ester]_0 - [ester] \qquad (4)$$

Table 1. Boiling points of esters and alcohols

| Compound	Boiling point (°C)	Literature value[6] (°C)
Methyl acetate	56·0–57·0	57·0
Ethyl acetate	75·8–76·5	77·06
n-Propyl acetate	101–102	101·6
n-Butyl acetate	125–126	126·5
n-Pentyl acetate	148–149	149·25
Ethyl fluoroacetate	120–122	121·7
Ethyl propanoate	98·0–98·8	99·10
Ethyl phenylacetate	222–224	227
Ethyl butanoate	119–120	121–126
Ethyl pentanoate	145–147	144·6 (736 mmHg)
Ethyl cyanoacetate	203–204	205
Ethyl dichloroacetate	152–153	155·5 (764 mmHg)
Ethyl trichloroacetate	166–168	168
Methanol	63·5–74·5	64·96
Ethanol	77–78	78·5
1-Propanol	96·5–97·5	97·4
1-Butanol	116–117	117·25
1-Pentanol	136–137	137·3
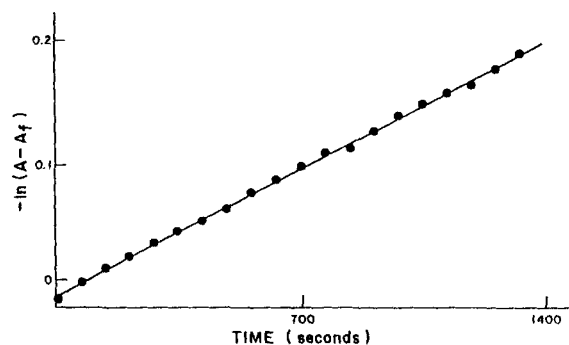
Figure 1. Typical pseudo-first-order rate plot for the oxidation of ethanol by chromium(VI). [Ethanol] = 0·102 M; $[Cr^{6+}]$ = 0·005 M; [HCl] = 1·49 M; temperature = 25·1 ± 0·1 °C. Slope = 0·0100 ± 0·002 s^{-1}; r = 0·9995

If the concentration of oxidant is small compared with the concentration of ester (5×10^{-4} and $0 \cdot 1$ M, respectively, in these reactions) the amount of ethanol consumed by oxidation would be insignificant.

Substitution of [ester] from equation (3) into equation (4) then gives

$$[\text{alcohol}] = [\text{ester}]_0(1 - e^{-k_H t}) \qquad (5)$$

The rate law for oxidation of the alcohol by chromic acid is given by the equation

$$-d[\text{Ox}]/dt = k_{ox}[\text{alcohol}][\text{Ox}] \qquad (6)$$

where [Ox] denotes the concentration of oxidant. The concentration of oxidant can be calculated by use of the equation

$$[\text{Ox}] = (A - A_p)/(\varepsilon_0 - \varepsilon_p) \qquad (7)$$

where A is the absorbance at time t, A_p is the absorbance of the products of the reaction, ε_0 is the molar absorptivity for CrO_3 at 363 nm and ε_p is the molar absorptivity for the products at the same wavelength.[9] Substitution for [Ox] in equation (6) gives

$$-dA/dt = k_{ox}[\text{Alcohol}](A - A_p) \qquad (8)$$

from which [alcohol] can be calculated from the equation

$$[\text{alcohol}] = (-dA/dt)/k_{ox}(A - A_p) \qquad (9)$$

Substitution of [alcohol] from equation (5) into equation (9) gives the equation

$$-dA/dt = k_{ox}[\text{ester}]_0(1 - e^{-k_H t})(A - A_p) \qquad (10)$$

which can be easily integrated:

$$\ln(A_0 - A_p)/(A - A_p) = kt + k/k_H(e^{-k_H t} - 1) \qquad (11)$$

where k is $k_{ox}[\text{ester}]$. Equation (10) can also be recast in a linear form:

$$-\ln[1 + (dA/dt)/k(A - A_p)] = k_H t \qquad (12)$$

The hydrolysis rate constant, k_H, can then be obtained (from a set of absorbance–time data) by linear regression using equation (12) or by non-linear regression using equation (11).

For esterifications, described by the equation

$$\text{ROH} + CH_3CO_2H \rightleftharpoons CH_3CO_2R + H_2O \qquad (13)$$

the use of aqueous acetic acid as solvent permits the rate of reaction to be defined in terms of a pseudo-first-order rate law, assuming that the reverse reaction can be neglected initially:

$$-d[\text{ROH}]/dt = k_E[\text{ROH}] \qquad (14)$$

If a small amount of oxidant is present, the rate of its reduction can be shown (as above) to be linearly related to k_E through the equation

$$\ln[1 + (-dA/dt)/k(A - A_p)] = k_E t \qquad (15)$$

RESULTS

Spectral scans obtained when a solution of ethanol reacts with chromic acid (Figure 2) are similar to those obtained when chromic acid is reduced as the hydrolysis of ethyl acetate occurs (Figure 3). The main difference is in the spacing of the scans taken at fixed time intervals. Because the concentration of ethanol is decreasing under the conditions in Figure 2, the scans become progressively closer together, whereas under the conditions in Figure 3, because the concentration of ethanol is increasing, the scans become further and further apart. In other words, the rate of reaction is steadily decreasing in Figure 2, but steadily increasing in Figure 3.
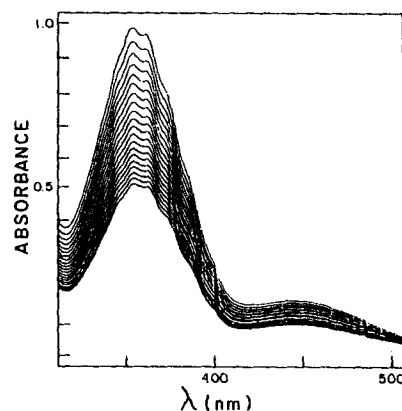

Figure 2. Sequential scans for the oxidation of ethanol by chromium(VI). Spectra taken at 100 s intervals (top to bottom). [Ethanol] = $0 \cdot 103$ M; [Cr^{6+}] = $0 \cdot 0005$ M; [HCl] = $1 \cdot 49$ M; temperature = $25 \cdot 1 \pm 0 \cdot 1$ °C
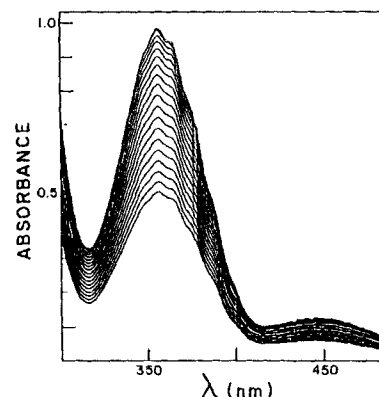

Figure 3. Sequential scans for the reduction of chromium(VI) by ethanol during the hydrolysis of ethyl acetate. [Ethyl acetate] = $0 \cdot 102$ M; [Cr^{6+}] = $0 \cdot 0005$ M; [HCl] = $1 \cdot 49$ M; temperature = $25 \cdot 1 \pm 0 \cdot 1$ °C

Table 2. Rate constants for the hydrolysis of esters

Ester	Acid solution	k_{ox} (l mol^{-1} s^{-1} × 10^3)[a]	k_H (s^{-1} × 10^4) Observed[a]	Literature value
Ethyl acetate	0·99 M HCl	1·28 ± 0·05	1·26 ± 0·06	1·2[b]
Ethyl acetate	1·49 M HCl	1·43 ± 0·04	1·66 ± 0·06	1·8[b]
Ethyl acetate	1·98 M HCl	1·43 ± 0·03	2·64 ± 0·01	2·6[b]
Ethyl acetate	2·97 M HCl	1·69 ± 0·02	4·52 ± 0·02	4·5[b]
Ethyl acetate	1·38 M H$_2$SO$_4$	8·7 ± 0·1	2·01 ± 0·04	2·01[b]
Ethyl acetate	2·11 M H$_2$SO$_4$	16·8 ± 0·4	3·06 ± 0·05	3·50[b]
n-Propyl acetate	14·1% H$_2$SO$_4$	9·4 ± 0·1	2·4 ± 0·1	2·4[c]
n-Propyl acetate	25·1% H$_2$SO$_4$	35 ± 5	5·7 ± 0·2	6·0[c]

[a] Values are averages of three or more experiments. Rate plots had correlation coefficients of 0·999 or better.
[b] Obtained by Bell et al.[10] using dilatometry.
[c] Obtained by Yates and McClelland[11] using a procedure that involves the quenching of aliquots.[12]

Table 3. Rate constants for the hydrolysis of alkyl acetates[a]

Alkyl acetate	k_{ox} (l mol^{-1} s^{-1})[b]	k_H (s^{-1} × 10^4)[b]	Relative rate Observed	Literature values[13]
Methyl acetate	0·040 ± 0·004	1·90 ± 0·05	0·57	0·58
Ethyl acetate	0·53 ± 0·01	1·08 ± 0·06	1·00	1·00
n-Propyl acetate	0·78 ± 0·03	0·97 ± 0·04	1·11	1·08
n-Butyl acetate	0·99 ± 0·03	0·92 ± 0·03	1·17	1·18
n-Pentyl acetate	1·03 ± 0·05	0·90 ± 0·01	1·20	

[a] Solvent, 50% (v/v) acetic acid containing 2·00 M HClO$_4$, temperature = 25 °C.
[b] Values are averages of three or more experiments. All rate plots had correlation coefficients of 0·999 or greater.

Rate constants, obtained from plots of $-\ln[1 + (dA/dt)/k(A - A_p)]$ vs time (Figure 4), were determined for the hydrolysis of ethyl and n-propyl acetate in aqueous HCl and H$_2$SO$_4$ (Table 2) and compared with those previously reported by others working

under the same conditions.[10–12] The relative rates of hydrolysis of alkyl acetates in aqueous acetic acid were also determined (Table 3) and compared with those reported in the literature.[13] The study was extended to include the hydrolysis of esters in aqueous perchloric acid solutions (Table 4) and in aqueous acetic acid solutions containing 2·00 M HClO$_4$ (Table 5).
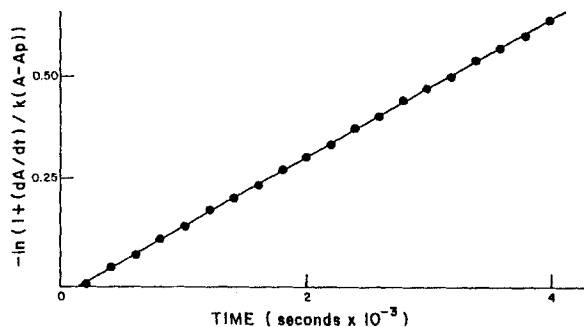

Figure 4. Typical plot for calculation of the hydrolysis rate constant. [Ethyl acetate] = 0·103 M; [CrO$_3$] = 0·0005 M; [HCl] = 1·49 M; temperature = 25·1 ± 0·1 °C. Slope = 0·0338 ± 0·0003 s^{-1}; r = 1·000

Table 4. Rate constants for the hydrolysis of ethyl acetate in perchloric acid solutions

[HClO$_4$] (M)	k_{ox} (l mol^{-1} s^{-1})[a]	k_H (s^{-1} × 10^4)[b]
1·00	0·0115 ± 0·0007	1·12 ± 0·02
1·40	0·0266 ± 0·0005	1·34 ± 0·02
2·00	0·070 ± 0·004	1·84 ± 0·03
2·40	0·128 ± 0·005	2·21 ± 0·02
3·00	0·29 ± 0·02	2·58 ± 0·04
3·40	0·44 ± 0·01	3·09 ± 0·09
4·00	0·92 ± 0·03	3·5 ± 0·1

[a] [Ethanol] = 0·103 M; [CrO$_3$] = 5 × 10^{-4} M; temperature = 25 °C.
[b] [Ethyl acetate] = 0·102 M, [CrO$_3$] = 5 × 10^{-4} M, temperature = 25 °C.

Table 5. Rate constants for the hydrolysis of esters in aqueous acetic acid solutions[a]

Ester	k_H (s^{-1} × 10^5)
Ethyl acetate	10·1 ± 0·1
Ethyl fluoracetate	6·7 ± 0·2
Ethyl propanoate	10·0 ± 0·1
Ethyl phenylacetate	4·1 ± 0·2
Ethyl butanoate	4·8 ± 0·1
Ethyl pentanoate	4·4 ± 0·1
Ethyl cyanoacetate	0·67 ± 0·02
Ethyl dichloroacetate	4·7 ± 0·1
Ethyl trichloroacetate	1·7 ± 0·3

[a] 50% (v/v) acetic acid; [HClO$_4$] = 2·00 M; [ester] ≈ 0·1 M; temperature = 25·0 ± 0·1 °C.

Table 6. Rate constants for the formation of alkyl acetates in acetic acid[a]

Alcohol	k_{ox} (l mol^{-1} s^{-1} × 10^3)	k_E (s^{-1} × 10^4)
Methanol	0·27 ± 0·02	10·5 ± 0·2
Ethanol	7·8 ± 0·3	4·4 ± 0·2
Propanol	10·3 ± 0·3	4·6 ± 0·2
Butanol	14·4 ± 0·5	4·8 ± 0·4
Pentanol	15·4 ± 0·6	4·6 ± 0·3
Nonanol	18 ± 1	3·21 ± 0·07

[a] 87% (v/v) acetic acid; [HCl] = 0·495 M; temperature = 25·0 ± 0·1 °C.

Table 7. Effect of acidity on the rate of esterification of ethanol in acetic acid[a]

[HCl] (M)	k_{ox} (l mol^{-1} s^{-1} × 10^3)	k_E (s^{-1} × 10^4)
0·099	7·9 ± 0·3	1·5 ± 0·1
0·198	9·6 ± 0·7	2·48 ± 0·03
0·297	10·9 ± 0·6	3·5 ± 0·1
0·396	12·2 ± 0·3	4·4 ± 0·1
0·495	10·5 ± 0·4	5·8 ± 0·1
0·594	12·0 ± 0·5	6·1 ± 0·2

[a] 90% (v/v) acetic acid; [ethanol] = 0·0857 M temperature = 25·0 ± 0·1 °C.

The versatility of this approach to reaction kinetics was further illustrated by a study of the rates of esterification reactions under conditions not previously accessible (Tables 6 and 7).

DISCUSSION

The approach described here provides workers with an additional way of determining reaction rates and rate constants for compounds that lack suitable chromophores. Although indirect, the method gives results
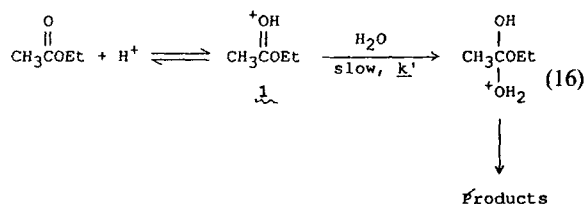
that seem to be reliable as judged from a comparison with rate constants previously determined in other laboratories using different techniques. Although the examples used to illustrate the method are limited to ester hydrolysis and formation, there seems to be little doubt that extensions to other reactions are possible; for example, the alkaline hydrolysis of alkyl halides to alcohols (using permanganate[14] or ruthenate[15] as assistant reagents), the formation of aldehydes or ketones (using 2,4-dinitrophenylhydrazine as the assistant reagent[16]), the formation of alkenes or alkynes (using permanganate or ruthenium tetroxide[17] as the assistant reagent), the reactions of amino acids (using ninhydrin as the assistant reagent[18]) or the reactions of aliphatic amines (using tetrachloro-*p*-benzoquinone as the assistant reagent[19]) should be amenable to study.

The primary requirements are that the assistant reagent does not interfere with the reaction under investigation and that it reacts with one of the products or reactants at a measurable rate under the conditions employed. Also, the rate constants obtained are more accurate when only one compound present in the reaction mixture reacts with the assistant reagent. In principle, it should be possible to use a reagent that reacts with more than one compound present; however, our experience with such systems has been that the resultant rate constants contain large uncertainties. Similarly, we have found that it is best to determine the rate constant for the reaction of the assistant reagent in separate experiments. Algorithms for determining both rate constants (e.g. k_{ox} and k_H) coincidentally from one experiment are available, but their use also results in an increase in the uncertainty of the calculated rate constants.

This approach permits the study of reaction rates under conditions that could not be easily tolerated by other methods. For example, it would be difficult to monitor the rate of formation of alkyl acetates in acetic acid (Table 6) by other methods currently available. Of course, the reaction conditions also impose severe limitations, e.g. hydrolysis under alkaline conditions could not be monitored using chromic acid as the assistant reagent because alcohols and CrO$_3$ do not react in basic solutions.[20] Under such conditions it should be possible, however, to use other oxidants such as permanganate[14] or ruthenate.[15] The best reagents to use for a particular reaction can be selected on the basis of known chemistry, but each application may require additional experimentation.

Although the purpose of this paper is to illustrate a new experimental method for the determination of reaction rates, it is also of interest to comment briefly on the significance of the results obtained with respect to reaction mechanisms. From the data reported in Table 4 it is possible to test quantitatively our current understanding of the way in which hydrolysis occurs. In

moderately acidic solutions it is expected that an $A_{Ac}2$ mechanism[21,22], as summarized in equation (16), will pertain.

$$CH_3COEt + H^+ \rightleftharpoons \overset{+OH}{\underset{\underset{\mathbf{1}}{\parallel}}{CH_3COEt}} \xrightarrow[slow, \underline{k'}]{H_2O} \overset{OH}{\underset{\underset{+OH_2}{\mid}}{CH_3COEt}} \quad (16)$$

$$\downarrow$$

$$Products$$

In perchloric acid solutions the available kinetic data seem to indicate that less than two molecules of water participate in the transition state.[22] However, from the data in Table 4 it is possible to make an independent calculation of the amount of water involved. Using previously reported pK_{BH^+} values,[23] the concentration of the conjugate acid of ethyl acetate, 1, can be calculated for each acidity from the Bunnett–Olson equation[24] or by use of the equations

$$\log([ester\ H^+]/[ester]) = -H_E + pK_{BH^+} \quad (17)$$

$$[ester] + [ester\ H^+] = [ester]_T \quad (18)$$

where H_E is the acidity function for esters (approximately equal to $0 \cdot 5H_0$),[23] $[ester]_T$ is the total concentration of ester, $[ester\ H^+]$ is the concentration of protonated ester and $[ester]$ is the concentration of unprotonated ester.

The expressions for the observed [equation (19)] and the derived rate laws [equation (20)] can be equated [equation (21)], rearranged into a linear form [equation (22)] and the value of n obtained from the appropriate plot (Figure 5).

$$rate = k_H[ester] \quad (19)$$

$$rate = k'[ester\ H^+]a_{H_2O}{}^n \quad (20)$$

$$k_H[ester] = k'[ester\ H^+]a_{H_2O}{}^n \quad (21)$$

$$\log k_H[ester]/[ester\ H^+] = n \log a_{H_2O} + \log k' \quad (22)$$

As can be seen n is very close to 2, as it is in sulfuric acid solutions.[11] It is not clear why these results are at variance with the previously reported value for n (1.63),[22] in perchloric acid solutions. However, the similarity between the value in H_2SO_4 and that for $HClO_4$ reported here is consistent with the contention
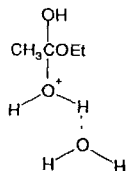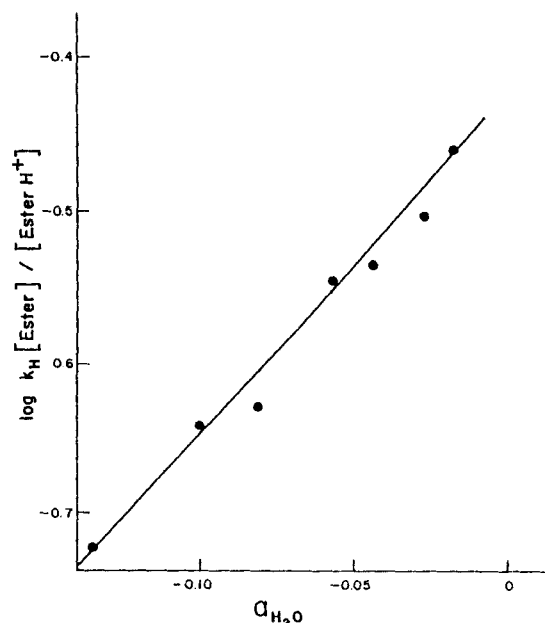
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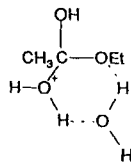
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Figure 5. Plot for determining the extent of water participation in the transition state. [Ethyl acetate] $= 0 \cdot 102$ M; temperature $= 25\,°C$. Slope $= 2 \cdot 16 \pm 0 \cdot 13$; $r = 0 \cdot 991$

made by Yates[22] that 'It seems inherently unlikely that the presence of different counterions such as HSO_4^-, ClO_4^- and Cl^- could alter the basic mechanism to such an extent that the role of water in the rate-determining step would be significantly changed.' The second molecule of water may be involved as a proton acceptor in either a linear[22] or cyclic[25] fashion as represented by structures 2 and 3.

The value of the rate constant for conversion of the conjugate acid, 1, into products, k', is approximately constant over the entire range of acidities studied, as indicated by the data in Table 8.

Table 8. Calculated values for k'

$[HClO_4]$ (M)	$[ester\ H^+]$ (M $\times 10^5$)[a]	k'[b]
$1 \cdot 00$	$3 \cdot 30$	$0 \cdot 376$
$1 \cdot 40$	$4 \cdot 36$	$0 \cdot 355$
$2 \cdot 00$	$6 \cdot 43$	$0 \cdot 357$
$2 \cdot 40$	$7 \cdot 91$	$0 \cdot 370$
$3 \cdot 00$	$1 \cdot 12$	$0 \cdot 340$
$3 \cdot 40$	$1 \cdot 38$	$0 \cdot 362$
$4 \cdot 00$	$1 \cdot 89$	$0 \cdot 350$

[a] $[Ester]_0 = 0 \cdot 102$ M; temperature $= 25\,°C$.
[b] $k' = k_H[ester]/([ester\ H^+]/a_{H_2O}{}^2)$.

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