The Hydrolysis of Methylene Diacetate and Ethylidene Diacetate in Concentrated Hydrochloric Acid Solutions

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Kinetic measurements have been made of the hydrolysis of methylene diacetate and ethylidene diacetate at 25°C in aqueous hydrochloric acid solutions at acid concentrations varying from 0.1 N up to 8 N. The results show that the velocity of the hydrolysis is more closely related to the acid concentration than to the acidity function of the reaction solution, thus indicating, in accord with the constitutional effects observed, that the hydrolysis of these esters takes place by a bimolecular mechanism, the transition state of which contains a water molecule in addition to the conjugate acid of the ester. No change of the reaction mechanism was observed even at the highest acid concentrations investigated.

In the previous study [1-4] the author established that the hydrolysis of simple alkoxymethyl esters, RCOOCH₂OR′, in aqueous acids takes place preferably by a unimolecular mechanism involving an intermediate formation of an alkoxymethyl cation, although under certain conditions a bimolecular mechanism which was considered to be essentially the same as that of simple alkyl esters, was also found to contribute to the reaction rate. The present paper gives the results of a kinetic study on the hydrolysis of constitutionally closely related compounds, methylene diacetate and ethylidene diacetate. Hammett's acidity function has been applied as a kinetic criterion of the molecularity of the rate-determining stage of the reaction, and for this the rate measurements have been extended up to high acid concentrations. The kinetics of the hydrolysis of these compounds by dilute aqueous acid solutions have been previously investigated by Skrabal and Schiffrer [5] and by Salmi [6].

RESULTS AND DISCUSSION

The method of following the rates of the hydrolysis reactions (R = H, Me)

$$(CH_3COO)_2CHR + H_2O \xrightarrow{H^+} RCHO + 2\ CH_3COOH$$
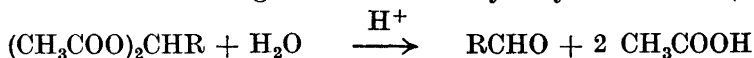
at various acid concentrations was based on the determination of formaldehyde or acetaldehyde produced during different reaction times. By this method it

was possible to extend the rate measurements up to about 8 N hydrochloric acid concentration. The results of the kinetic measurements are given in Tables 1 and 2. In the tables the values of $\bar{k}$ denote the first-order rate constants directly measured, the values of k giving the second-order rate constants which have been obtained by dividing the first-order rate constants by the concentrations of the catalyst hydrochloric acid. The tables also include the values of the Hammett acidity function H_0 for the solutions employed. These values have been obtained by interpolation from the data given by Hammett and Deyrup[7] and by Bell, Dowling and Noble[8].

The values obtained for the rate constants at relatively low acid concentrations are in good agreement with the corresponding values determined earlier by Skrabal and Schiffrer[5] and by Salmi[6]. The first authors found for the second-order rate constants at 25°C the following values: 0.000134 l mole⁻¹

Table 1. The hydrolysis of methylene diacetate by aqueous hydrochloric acid at 25 °C.

[HCl]	$10^4 \cdot \bar{k}$ sec.⁻¹	$10^4 \cdot k$ l mole⁻¹sec.⁻¹	H_0
0.1020	0.140	1.37	+ 1.06
0.396	0.550	1.39	+ 0.36
0.792	1.13	1.43	+ 0.02
1.188	1.80	1.52	− 0.19
1.584	2.56	1.62	− 0.36
1.980	3.29	1.66	− 0.53
2.376	4.22	1.78	− 0.68
3.168	6.18	1.95	− 0.98
3.96	8.23	2.08	− 1.28
4.75	11.9	· 2.50	− 1.57
5.94	18.2	3.06	− 1.98
7.13	27.1	3.80	− 2.47
7.92	33.2	4.19	− 2.84

Table 2. The hydrolysis of ethylidene diacetate by aqueous hydrochloric acid at 25°C.

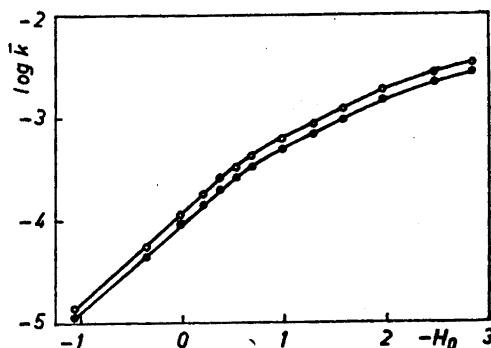| [HCl]	$10^4 \cdot \bar{k}$ sec.⁻¹	$10^4 \cdot k$ l mole⁻¹sec.⁻¹	H_0
0.1020	0.114	1.12	+ 1.06
0.396	0.444	1.12	+ 0.36
0.792	0.920	1.16	+ 0.02
1.188	1.41	1.19	− 0.19
1.584	2.01	1.27	− 0.36
1.980	2.58	1.30	− 0.53
2.376	3.22	1.36	− 0.68
3.168	5.04	1.59	− 0.98
3.96	6.92	1.75	− 1.28
4.75	9.70	2.04	− 1.57
5.94	14.6	2.46	− 1.98
7.13	22.0	3.09	− 2.47
7.92	27.6	3.48	− 2.84

Fig. 1. The plots of the logarithms of the first-order rate constants against $-H_0$. Aqueous hydrochloric acid, 25°C. Upper curve, the hydrolysis of methylene diacetate; lower curve, the hydrolysis of ethylidene diacetate.

sec.$^{-1}$ for methylene diacetate, and 0.000108 l mole^{-1}sec.$^{-1}$ for ethylidene diacetate, respectively. Salmi determined the value 0.000144 l mole^{-1}sec.$^{-1}$ for the hydrolysis of methylene diacetate at 25°C.

A comparison between the values of Tables 1 and 2 shows that the hydrolysis rates of methylene diacetate and ethylidene diacetate are similarly influenced by the acid concentration of the solution, the rate constants of the former compound being slightly higher than those of the latter at the same acid concentrations. In both cases the second-order rate constants increase slightly when passing over to higher acid concentrations, the relative increases being, however, of a much lower order of magnitude than those observed by alkoxymethyl esters [1].

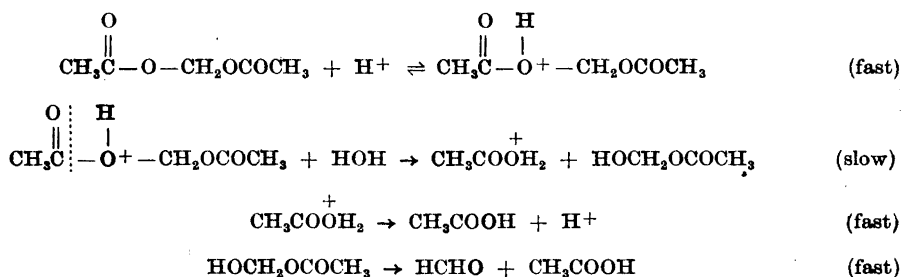Fig. 1 gives the plots of the logarithms of the first-order rate constants against the Hammett acidity function. The plots show that the values of log $\bar{k}$ increase much less rapidly than the values of $-H_0$, when passing up to higher acid concentrations, thus considerably differing from the behaviour observed by alkoxymethyl esters [1]. *E. g.*, in the case of methylene diacetate, a linear relation between log $\bar{k}$ and $-H_0$ with a slope of unity would imply an about 8 000-fold increase in the first-order rate constant, when passing from 0.1020 N up to 7.92 N hydrochloric acid, and even a larger increase were to be expected, if the dependence of log $\bar{k}$ on the acidity function were similar to that observed by methoxymethyl and ethoxymethyl acetates. The actual increase in the value of $\bar{k}$ is, however, much lower in magnitude, *viz.* 240-fold (Table 1).

On the contrary, the results for the diacetates show a close similarity to the observations made by Bell, Dowling and Noble [8] of the hydrolysis of methyl formate and ethyl acetate by concentrated hydrochloric acid solutions. These authors found the first-order rate constants to increase slightly more rapidly than the acid concentration of the solution. The increase was, however, too small to be interpreted in terms of the acidity function of the solution. It was considered that the results are in a satisfactory agreement

with the bimolecular mechanism of the acid-catalysed ester hydrolysis, in view of the fact that there is no reason to assume that the hydrolysis velocity would remain strictly proportional to the acid concentration, when going up to relatively high acid concentrations.

The fact that the esters investigated here are affected by the acid concentration of the reaction solution similarly as the simple alkyl esters indicates that both the reactions take place by an essentially similar mechanism. As the hydrolysis velocity of the diacetates is also more closely related to the acid concentration than to the value of H_0 of the reaction solution, it implies that the reaction is bimolecular, *i. e.* the critical complex contains a water molecule which is undergoing a change of covalency, in addition to the conjugate acid of the substrate, *cf.* Ref.[1]

Although the rate measurements at high acid concentrations furnish only a criterion of molecularity of the rate-determining reaction stage, and do not allow a distinction as to the point of the initial bond rupture, there are no reasons to support an assumption that this point would not be the same here as in the acid-catalysed hydrolysis of simple alkyl esters, *i. e.* the acyl-oxygen bond [9]. Owing to the less electrophilic character of the carbon atom of the methylene or ethylidene group, in comparison to that of the carbonyl group, a bimolecular alkyl-oxygen fission mechanism would be less probable, as also shown by the fact that this type of mechanism has never been established in acid-catalysed ester hydrolysis. The bimolecular acyl-oxygen fission mechanism [9], as particularised to the hydrolysis of methylene diacetate

$$CH_3\overset{\overset{O}{\|}}{C}-O-CH_2OCOCH_3 \ + \ H^+ \ \rightleftharpoons \ CH_3\overset{\overset{O}{\|}\ \overset{H}{|}}{C}-O^+-CH_2OCOCH_3 \qquad \text{(fast)}$$

$$CH_3\overset{\overset{O}{\|}\ \overset{H}{|}}{C}-O^+-CH_2OCOCH_3 \ + \ HOH \ \rightarrow \ CH_3\overset{+}{C}OOH_2 \ + \ HOCH_2OCOCH_3 \qquad \text{(slow)}$$

$$CH_3\overset{+}{C}OOH_2 \ \rightarrow \ CH_3COOH \ + \ H^+ \qquad \text{(fast)}$$

$$HOCH_2OCOCH_3 \ \rightarrow \ HCHO \ + \ CH_3COOH \qquad \text{(fast)}$$

is also in accord with the constitutional effects. The values of k determined for the hydrolysis of methylene diacetate and ethylidene diacetate at relatively low acid concentrations at 25°C (Tables 1 and 2) are of the same order of magnitude as the corresponding value for methyl acetate, 0.000109 1 mole^{-1}sec.$^{-1}$, determined by Tommila and Hella [10]. This is well understood in view of the fact that the velocity of the acid-catalysed ester hydrolysis by the bimolecular mechanism is but slightly influenced by substituents on the alkyl group of the ester.

It might be suggested that the small increase in the values of the second-order rate constants with acid concentration (Tables 1 and 2) is due, at least partly, to a simultaneous unimolecular mechanism which is greatly favoured by the high proton-availability of the concentrated acid solutions, *cf.* Ref.[4] This assumption is, however, rendered doubtful by the following reasons. The

cation formed in the rate-determining unimolecular reaction stage could be presented as (cf. Ref.[1]) $CH_3COOCHR$ (R = H, Me). The unimolecular reaction would be greatly accelerated by an electron-releasing substituent directly attached to the site of reaction, i. e. that carbon atom, which acquires a positive charge on the attainment of the transition state. The influence of this effect is illustrated, for instance, by the unimolecular solvolysis of 1-chloroethers where it was established [11] that the rate-determining formation of the cation CH_3OCHCH_3 is greatly more rapid than that of the cation CH_3OCH_2. Thus the conditions for the unimolecular mechanism are much more favourable in the hydrolysis of ethylidene diacetate than in that of methylene diacetate, and hence a change of the reaction mechanism, when passing up to higher acid concentrations, would occur by the former compound earlier than by the latter. If such a change of mechanism were actually present here, the values of the rate constants of ethylidene diacetate would increase in comparison to the corresponding values of methylene diacetate, when higher acid concentrations are approached. As shown by Fig. 1, however, the relative hydrolysis velocities of both the diacetates remain practically unaffected by the acid concentration of the reaction solution, thus indicating that the reaction mechanisms remain bimolecular even at the highest acid concentrations investigated.

EXPERIMENTAL

Materials. Methylene diacetate, $(CH_3COO)_2CH_2$, and ethylidene diacetate, $(CH_3COO)_2CHCH_3$, were prepared by the method described by Knoevenagel [12]. The raw products were purified by repeated fractional distillations. The boiling points were: 88.5°C/40 mm Hg for methylene diacetate, and 166.5—167.0°C/752 mm Hg for ethylidene diacetate, respectively. The purity of the products was controlled by hydrolysing weighed samples by alkali (one minute was found to be sufficient for a quantitative hydrolysis of the esters by a large excess of 0.25 N sodium hydroxide solution), and after neutralisation, by determining the aldehyde formed using the previous method [11,13]. The standard iodine solution used for the aldehyde determinations was 0.0688 N. In the analysis of formaldehyde formed by the hydrolysis of methylene diacetate, a sample of 45.6 mg of the ester was equivalent to 10.17 ml of the standard iodine solution (calc. 10.03 ml), and a sample of 66.2 mg was equivalent to 14.70 ml of the iodine solution (calc. 14.57 ml). In the analysis of acetaldehyde formed by the hydrolysis of weighed samples of ethylidene diacetate, respectively, 43.5 mg of the ester was equivalent to 8.76 ml of the standard iodine solution (calc. 8.65 ml), and 60.7 mg was equivalent to 12.16 ml of the standard solution (calc. 12.07 ml).

Kinetic measurements. The preparation of the reaction solutions and the method of kinetic measurements were similar to those described in connection with the earlier work on the hydrolysis of alkoxymethyl esters [1]. In all cases the first-order kinetics were well obeyed. Tables 3 and 4 give the details for two typical examples of the individual rate

Table 3. The hydrolysis of methylene diacetate in 7.92 N hydrochloric acid at 25°C.
a = 0.0440.

t (in minutes)	1	2	3	4	5	6	8	10
$10^2 (a-x)$	3.59	2.97	2.42	2.04	1.65	1.31	0.87	0.60
$10^3 \cdot \bar{k}$	3.39	3.27	3.32	3.20	3.27	3.37	3.38	3.32

Average $\bar{k}$ = 0.00332 sec.$^{-1}$

Table 4. The hydrolysis of ethylidene diacetate in 5.94 N hydrochloric acid at 25°C.

$$a = 0.0503.$$

t (in minutes)	2	4	6	8	10	12	14	16
$10^2 (a-x)$	4.25	3.53	2.94	2.54	2.10	1.75	1.48	1.24
$10^3 \cdot \bar{k}$	1.40	1.48	1.49	1.42	1.46	1.47	1.46	1.46

Average $\bar{k} = 0.00146$ sec.$^{-1}$

measurements. In the tables, a denotes the ester concentration at zero time (at the time of taking the first sample), $(a-x)$ the ester concentration remaining at time t, and $\bar{k}$ the first-order rate constant, respectively.

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