

### 320. *Kinetics of the Acid-catalysed Hydrolysis and Decomposition of Ethylidene Diacetate.*

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The kinetics of the hydrolysis of ethylidene diacetate have been studied in aqueous hydrochloric acid up to an acid concentration of 8.9M. The reaction velocity follows the acid concentration more closely than it does the acidity function, thus showing the same behaviour as the hydrolysis of simple esters. It is concluded that the two reactions proceed by similar mechanisms, and that the hydrolysis of ethylidene diacetate does not involve preliminary decomposition into acetaldehyde and acetic anhydride.

The decomposition of ethylidene diacetate in chlorobenzene is catalysed by trichloroacetic acid and by stannic chloride, the reaction velocity being proportional to the first power of the catalyst concentration. Under the same conditions stannic chloride is more effective than trichloroacetic acid by a factor of about 15,000.

ETHYLIDENE DIACETATE is hydrolysed in aqueous solution to acetaldehyde and acetic acid, the reaction being of the first order with respect to the ester, and catalysed by hydrogen ions and hydroxyl ions.<sup>1</sup> In the absence of water it undergoes thermal decomposition in the range 200—300° to acetaldehyde and acetic anhydride by a homogeneous unimolecular gas reaction.<sup>2</sup> Bell and Burnett<sup>3</sup> were unable to detect acid catalysis in the gaseous decomposition; however, ethylidene diacetate is commonly prepared from acetaldehyde and acetic anhydride at low temperatures by means of Lewis-acid catalysts such as ferric bromide, and it therefore seems probable that the decomposition in the absence of water will also exhibit acid catalysis under suitable conditions.

The above behaviour resembles that of the structurally similar paraldehyde, which

<sup>1</sup> Skrabal, *Z. phys. Chem.*, 1926, **122**, 357; 1927, **128**, 457.

<sup>2</sup> Coffin, *Canad. J. Res.*, 1932, **7**, 75.

<sup>3</sup> Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 474.

decomposes to acetaldehyde by a homogeneous gas reaction,<sup>4,5</sup> by an acid-catalysed heterogeneous gas reaction,<sup>6</sup> and by an acid-catalysed homogeneous reaction both in water<sup>7</sup> and in non-aqueous solvents.<sup>8,9</sup> In concentrated aqueous solutions of acids the rate of depolymerisation of paraldehyde is more closely parallel to the acidity function than to the hydrogen-ion concentration, and this may be regarded as evidence that (even in aqueous solution) the rate-determining step does not involve a water molecule:<sup>7</sup> the same is true of the hydrolysis of dimethoxymethane.<sup>10</sup> The hydrolysis of ethylidene diacetate might follow a similar course: on the other hand, it also resembles the simple carboxylic esters, for which the rate of acid hydrolysis follows the acid concentration rather than the acidity function,<sup>11</sup> thus supporting the generally accepted mechanism<sup>12</sup> with a water molecule in the transition state.

Skrabal's measurements<sup>1</sup> on the acid hydrolysis of ethylidene diacetate extend only up to 1M-acid, at which concentration there is little difference between the acidity function and the hydrogen-ion concentration. We have therefore made measurements in the range 0.3—9M-aqueous hydrochloric acid, and have also investigated briefly the acid-catalysed decomposition in chlorobenzene.

#### EXPERIMENTAL

Ethylidene diacetate was a commercial sample containing less than 0.1% of free acetaldehyde. Its purity was estimated as 95—97% by complete hydrolysis to acetaldehyde and titration of the latter as described below. The remaining 3—5% was shown to be mainly acetic anhydride by hydrolysing it in neutral solution (which does not affect the ester) and titrating the acetic acid with sodium hydroxide. Attempts to purify the ester by distillation produced no improvement (probably because of further thermal decomposition), and since it was shown later that the addition of acetic anhydride had no effect on the kinetics the original sample was used without purification. Hydrochloric acid, trichloroacetic acid, and stannic chloride were "AnalaR" products, the first being standardised against recrystallised borax. Chlorobenzene was dried (CaCl<sub>2</sub> then P<sub>2</sub>O<sub>5</sub>) and distilled.

In all the kinetic measurements the acetaldehyde produced was estimated by Friedemann, Cotonio, and Shaffer's method.<sup>13</sup> For the measurements in aqueous solution 50 c.c. of solution 0.02—0.03M in ester were kept at 25° and at intervals a 2 c.c. sample was run into 5 c.c. of 0.2M-sodium hydrogen sulphite solution. After 15 min. most of the excess of hydrogen sulphite was removed with 0.25N-iodine solution, and the remainder by titration with 0.015N-iodine solution (starch). The aldehyde-bisulphite compound was then decomposed by adding 1 g. of solid sodium hydrogen carbonate, and the hydrogen sulphite liberated titrated with 0.015N-iodine solution. At the higher acid concentrations (>4.0M) it was necessary to neutralise some of the acid in the sample by adding sodium hydroxide (and ice) to the sodium hydrogen sulphite solution.

In aqueous hydrochloric acid the hydrolysis was kinetically of the first order during 90% of its course, and the velocity constants were determined graphically by plotting  $\log(C_\infty - C_t)$  against  $t$ , where  $C_t$  is the concentration of acetaldehyde after time  $t$ . The value of  $C_\infty$  was calculated from the weight of ester taken. The velocity constants are collected in Table 1.

Catalysis in non-aqueous solution was studied in less detail, the object being to establish the general character of the decomposition under these conditions. The analytical method used for following the reaction was the same as for aqueous solutions. For each catalyst concentration a number of samples were sealed in glass bulbs, and analysed at intervals.

<sup>4</sup> Coffin, *Canad. J. Res.*, 1931, **5**, 636.

<sup>5</sup> Bell and Burnett, *Trans. Faraday Soc.*, 1938, **34**, 420.

<sup>6</sup> *Idem, ibid.*, 1937, **33**, 355.

<sup>7</sup> Bell and Brown, *J.*, 1954, 774.

<sup>8</sup> Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1792.

<sup>9</sup> Bell and Skinner, *J.*, 1952, 2955.

<sup>10</sup> McIntyre and Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240.

<sup>11</sup> Bell, Dowling, and Noble, *J.*, 1955, 3106.

<sup>12</sup> Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686.

<sup>13</sup> Friedemann, Cotonio, and Shaffer, *J. Biol. Chem.*, 1927, **73**, 342.

Catalysis by trichloroacetic acid in chlorobenzene was studied at 100°, and in preliminary experiments the reaction velocity was found to fall off with time more rapidly than corresponded to a first-order reaction. Tests showed that this behaviour was not primarily due to reversibility of the decomposition or to polymerisation of the acetaldehyde produced, but could be attributed mainly to the reaction  $(\text{CH}_3\cdot\text{CO})_2\text{O} + 2\text{CCl}_3\cdot\text{CO}_2\text{H} \longrightarrow (\text{CCl}_3\cdot\text{CO})_2\text{O} + 2\text{CH}_3\cdot\text{CO}_2\text{H}$ , which replaces the trichloroacetic acid by the much less effective acetic acid. Thus if a trichloroacetic acid solution was heated to 100° with an equivalent amount of acetic anhydride before use its catalytic power was found to be greatly diminished. In order to minimise this complication a low concentration of ester was used (<0.01M) and only the first 50% of each reaction was followed: the velocity constants given in Table 2 are therefore less accurate than those for aqueous solutions.

TABLE 1. *Hydrolysis of ethylidene diacetate in aqueous hydrochloric acid at 25°.*

<i>c</i> = acid concn. (M) *; <i>k</i> = first-order velocity constant (sec. <sup>-1</sup> ).								
<i>c</i> .....	0.330	0.391	0.489	0.713	1.129	1.614	2.26	3.39
<i>H</i> <sub>0</sub> .....	0.44	0.38	0.28	0.11	-0.14	-0.40	-0.63	-1.04
10 <sup>4</sup> <i>k</i> .....	3.58	4.50	5.43	7.58	11.5	19.5	30.5	54.2
<i>c</i> .....	4.51	4.52	6.54	8.08	8.28	8.73	8.88	
<i>H</i> <sub>0</sub> .....	-1.46	-1.46	-2.26	-2.89	-2.96	-3.12	-3.14	
10 <sup>4</sup> <i>k</i> .....	87.2	82.3	145	221	277	356	333	

TABLE 2. *Decomposition of ethylidene diacetate in chlorobenzene.*

<i>c</i> = catalyst concn. (M); <i>k</i> = first-order velocity constant (sec. <sup>-1</sup> ).								
(a) Solutions of trichloroacetic acid at 100°.								
<i>c</i> .....	0.0874	0.133	0.205	0.375	0.417	0.457	0.692	1.04
10 <sup>4</sup> <i>k</i> .....	1.1	1.2	2.1	3.9	4.4	5.2	9.3	19
(b) Solutions of stannic chloride at 25°.								
<i>c</i> .....	0.00529	0.00821	0.0181	0.0199	0.0266	0.0314	0.0407	0.0417
10 <sup>4</sup> <i>k</i> .....	2.5	8.1	21	23	29	30	45	46

Dilute solutions of stannic chloride in chlorobenzene were found to decompose the ester rapidly at 25°. (The presence of the stannous-stannic redox system made it necessary to modify the method of analysis as described by Bell and Skinner.<sup>9</sup>) There were again considerable departures from first-order behaviour, in this case probably because the decomposition is appreciably reversible under these conditions. The results given in Table 2 were obtained by using dilute ester solutions (<0.01M) and correspond to the first 20—30% of the reaction.

## DISCUSSION

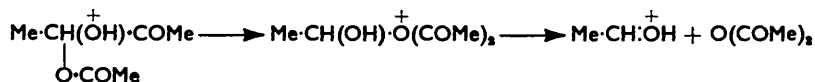
The results in aqueous hydrochloric acid (Table 1) lead to the most definite conclusions about the mechanism of the reaction. The Figure shows a plot of  $\log_{10}k$  against  $H_0$  or  $\log_{10}c$ , the values of  $H_0$  being taken from Hammett's measurements<sup>14</sup> as extended by Bell, Dowding, and Noble.<sup>11</sup> The straight line is drawn with unit slope. It is clear that the relation to  $H_0$  is far from linear, while the curve relating  $\log_{10}k$  to  $\log_{10}c$  has an upward curvature closely resembling that found for the hydrolysis of simple esters.<sup>11</sup> (This curvature is diminished if the concentration is expressed in moles per kg. of solvent rather than per litre of solution.) This is good evidence that the hydrolysis of ethylidene diacetate in aqueous solution proceeds by the same mechanism as the hydrolysis of simple esters, and does not involve a slow decomposition into acetaldehyde and acetic anhydride followed by rapid hydration of the latter.

The results in chlorobenzene solution (Table 2) show that the decomposition is catalysed both by proton acids and by Lewis acids. The function of the acid catalyst may be to lower the activation energy needed for the electronic rearrangement involved (by giving a

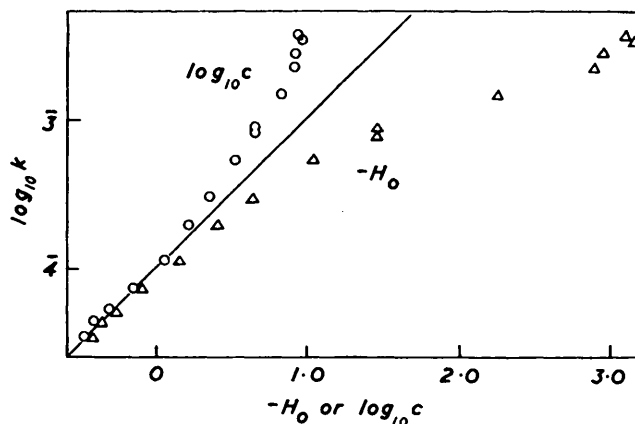
\* Throughout this paper we emphasise that M (molar) has its usual meaning of moles of solute per litre of solution (see *J.*, 1955, 4498).

<sup>14</sup> Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, 56, 830.

positive charge to one of the acyl oxygen atoms): alternatively, it is possible to formulate a mechanism in two steps,



which is closely analogous to that suggested for the decomposition of paraldehyde.<sup>7</sup> Table 2 shows that for the reaction studied here the velocity is proportional to the first power of the acid concentration, in contrast with the power of approximately two found



for the decomposition of paraldehyde in non-aqueous solvents.<sup>8,9</sup> The difference probably depends on the fact that the paraldehyde molecule contains three equivalent oxygen atoms, and that the most efficient mode of decomposition involves the attack on two of them by catalyst molecules.

The results in Table 2 do not permit any direct comparison of the catalytic powers of trichloroacetic acid and stannic chloride because of the difference in temperature. Two experiments with trichloroacetic acid at 25° gave an approximate value of  $k = 9 \times 10^{-7} \text{ sec.}^{-1}$  for a 1M-catalyst concentration, showing that stannic chloride is about 15,000 times more effective than trichloroacetic acid: this resembles the behaviour of Lewis acids and proton acids in the decomposition of paraldehyde.<sup>9</sup> By combining the velocity constants for trichloroacetic acid at 25° and 100° we find  $E \approx 18 \text{ kcal./mole}$ ,  $A \approx 10^7 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  for the parameters of the Arrhenius equation. The value of  $A$  is less than the collision-theory value by a factor of about  $10^4$ , as is commonly found for reactions between uncharged molecules which proceed by an ionic mechanism.