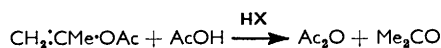


**554. Acylation. Part XII.\*** *A Comparison of Acid-catalysed Acetylation by Isopropenyl Acetate, Cyclohexenyl Acetate, and  $\alpha$ -Acetoxystyrene.*

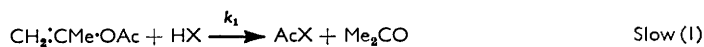
By E. A. JEFFERY and D. P. N. SATCHELL.

Kinetic analysis shows that the acid-catalysed acetylations of acetic acid by isopropenyl acetate, cyclohexenyl acetate, and  $\alpha$ -acetoxystyrene proceed by similar mechanisms. The mechanism previously established for isopropenyl acetate is therefore probably common to most vinyl acetates. The rate of the first step—the reaction of vinyl acetate with catalyst—is shown to depend on both the acidic strength of the catalyst and the nucleophilicity of its conjugate base.

PART III<sup>1</sup> of this series dealt with acid-catalysed acetylation of acetic acid by isopropenyl acetate. The products are acetone and acetic anhydride. In an excess of acetic acid the reaction goes to completion. A variety of catalysts (HX) were used, including hydrogen chloride, toluene-*p*-sulphonic acid, and perchloric acid.



Our kinetic analysis led us to the following reaction mechanism:

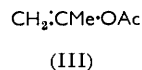
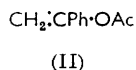
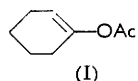


For hydrogen halides, equilibrium (2) lies well to the left but for the other catalysts it lies to the right. As a result, the appearance of the products takes a different kinetic form in the two cases. The main purpose of the experiments described in this paper was

\* Part XI, *J.*, 1963, 2889.

<sup>1</sup> Jeffery and Satchell, *J.*, 1962, 1876.

to discover whether other vinyl acetates display similar kinetic behaviour. It was felt also that a comparison of the values of  $k_1$  for different acetates would throw light on the details of step (I), about which little definite could be said in Part III. We have compared the behaviour of cyclohexenyl acetate (I) and of  $\alpha$ -acetoxystyrene (II) with that of isopropenyl acetate (III). The substrate acetylated has again been acetic acid. The products from the acetates (I) and (II) are cyclohexanone and acetophenone, respectively, together with acetic anhydride.



*Catalysis by Hydrogen Chloride.*—Both the acetates (I) and (II) show behaviour analogous to that of (III). The rate of formation of the products bears no simple relation to the stoichiometric concentrations of the reactants and catalyst. Equation (6) of Part III is obeyed. Plots of  $\frac{1}{t} \log B_0/(B_0 - A)$  against  $A/B_0 t$  for acetates (I) and (II) were excellent straight lines.  $B_0$  is the initial acetate concentration, and the other symbols throughout this paper retain their previous meanings.<sup>1</sup> Values of  $P$  and  $QB_0/C$  are in Table 1. The kinetic effect of acetic anhydride added initially was predictable [as for

TABLE 1.

Values of  $P$  and  $Q$  obtained from plots of equation (6) of Part III for the hydrogen chloride-catalysed reactions. Units are as in Part III.

$B_0$	$10^2 C$	$P$	$10^4 Q$	$10^2 QB_0/C$	$B_0$	$10^2 C$	$P$	$10^4 Q$	$10^2 QB_0/C$
<i>Cyclohexenyl acetate.</i>					<i><math>\alpha</math>-Acetoxystyrene (II).</i>				
0.528	1.36	0.415	0.87	3.38	0.541	0.625	0.362	0.85	7.37
0.357	1.39	0.425	1.35	3.47	0.411	0.638	0.359	1.90	7.51
0.329	2.09	0.425	1.95	3.07	0.283	0.169	0.340	0.45	7.52
0.304	0.417	0.415	0.44	3.21	0.280	0.335	0.350	0.82	6.83
0.290	0.755	0.416	0.87	3.35	0.273	0.652	0.345	1.70	7.10
0.139	0.778	0.402	1.93	3.45	0.261	1.25	0.350	3.25	6.78
					0.130	0.666	0.345	3.20	6.25

(III), see equation (8) of Part III], the values of  $P$  and  $QB_0/C$  being insignificantly altered. Average values of  $k_2$ ,  $k_1/k_{-2}$  and  $k_1/K$  (where  $K = k_{-2}/k_2[\text{AcOH}]$ ) for the acetates (I), (II), and (III) are compared in Table 2. The quantities directly determined are  $k_1/K$  and  $k_1/k_{-2}$ ;  $k_2$  is calculated from these. The agreement between the calculated values of  $k_2$

TABLE 2.

Hydrogen chloride-catalysed acetylation of acetic acid by substituted vinyl acetates at 40°.  $K$ ,  $k_1$ ,  $k_2$ ,  $k_{-2}$  are defined in the text.

Acetate	$k_1/k_{-2}$	$k_1/K$	$k_2$
Isopropenyl acetate .....	0.361	0.265	0.0457
$\alpha$ -Acetoxystyrene .....	0.201	0.163	0.0492
Cyclohexenyl acetate .....	0.010 *	0.0076	0.0475 *

\* See text.

for acetates (II) and (III) is impressive. For (I),  $k_1/k_{-2}$  is so small that its accurate estimation (from  $P$ ) is impossible. An independent value of  $k_2$  is therefore not obtainable in this case. If an average value (0.0475) is taken from the results for acetates (II) and (III), since  $k_1/K$  is known,  $k_1/k_{-2}$  for (I) may be calculated accurately.

*Catalysis by Toluene-p-sulphonic and Perchloric Acid.*—As for isopropenyl acetate (III), the acetates (I) and (II) showed simple kinetic behaviour with these catalysts. Equation (11) of Part (III) is obeyed and only  $k_1$  is determined. Our results are in Table 3.

*Conclusions.*—(i) The general similarity in the kinetic behaviour of all three compounds indicates that most, if not all, vinyl acetates effect acetylation by a mechanism similar to that we have previously established for isopropenyl acetate (III), *i.e.*, equations (1) and (2).\*

(ii) Apart from the good agreement (already noted) between the values of  $k_2$  found with the acetates (II) and (III), a significant feature of the results in Tables 2 and 3 is the

TABLE 3.

Perchloric and toluene-*p*-sulphonic acid-catalysed acetylation of acetic acid by substituted vinyl acetate at 40°.

Acetate	$k_1$	
	$p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$	$\text{HClO}_4$
Isopropenyl acetate .....	1.70	47.5
$\alpha$ -Acetoxystyrene .....	0.932	5.48
Cyclohexenyl acetate .....	0.0644	—

relatively low reactivity of cyclohexenyl acetate (I). The relative reactivities of the three compounds in attacking the catalyst (compare  $k_1$  or  $k_1/K$ ) are roughly the same for both hydrogen chloride and toluene-*p*-sulphonic acid, but whereas  $\alpha$ -acetoxystyrene (II) is about half as reactive as isopropenyl acetate (III), the cyclohexenyl ester (I) has only about one thirty-fifth of the reactivity of (III).

Step (1), the addition of the catalyst to the vinyl acetate, doubtless involves an initial protonation of some form. There are three potential sites: the carbonyl-oxygen atom, the ethereal oxygen atom, and the methylene group (or its associated double bond). In Part III we were unable to distinguish clearly between these possibilities. We now suggest that the most marked difference between the cyclohexenyl ester (I) and the other two, so far as these protonation sites are concerned, is the endocyclic nature of its carbon-carbon double bond. Moreover, cyclohexene is known<sup>4</sup> to undergo acid-catalysed hydration more (perhaps considerably more) slowly than propene. We feel, therefore, that the relative reactivities of the three esters point to the conclusion that the important protonation occurs primarily at carbon (or at the carbon-carbon double bond). This conclusion is in agreement with that of other workers<sup>5</sup> concerning related compounds.

(iii) The similarity of the relative reactivities with hydrogen chloride and toluene-*p*-sulphonic acid implies the absence of steric effects in step (1) dependent on these catalysts.

(iv) With catalysts which provide simple kinetic behaviour (*e.g.*, perchloric, toluene-*p*-sulphonic acid, etc.; see Part III) the magnitude of  $k_1$  for a given acetate increases with the conventional acidity of the catalyst (see Table 3). However,  $K$  probably<sup>6</sup> has a value of at least 50. This means that the values of  $k_1$  for hydrogen chloride catalysis must be notably greater than those for toluene-*p*-sulphonic acid, an acid of very similar strength in acetic acid.<sup>7</sup> The acid strength of the catalyst is therefore not its only significant property in the reaction. Indeed the kinetic nucleophilicity of its conjugate anion seems likely to be an important factor, for the completion of step (1) must involve nucleophilic attack by the anion on the carbonyl-carbon atom. If step (1) comprises a fast pre-equilibrium involving the acid, followed by a slow anionic attack, then catalysts of

\* The parent compound, vinyl acetate, yields, not acetaldehyde and acetic anhydride, but ethylidene diacetate.<sup>2</sup> In this case therefore the primary products react further, as is to be expected.<sup>3</sup>

<sup>2</sup> Rothman, Serota, Pearlstein, and Swern, *J. Org. Chem.*, 1962, **27**, 3123.

<sup>3</sup> *E.g.*, Wegscheider and Spath, *Monatsh.*, 1909, **30**, 825; Isikawa and Matsuo, *Reports Sci. Res. Inst. Japan*, 1952, **23**, 307.

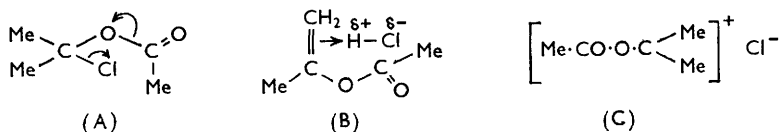
<sup>4</sup> R. S. Satchell, Thesis, London, 1962.

<sup>5</sup> Wasserman and Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 611, 1411; Euranto and Kujanpaa, *Acta Chem. Scand.*, 1961, **15**, 1209.

<sup>6</sup> Satchell, *J.*, 1960, 1752.

<sup>7</sup> Koltzoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

comparable thermodynamic strength (hydrogen chloride and toluene-*p*-sulphonic acid) but with anions of different nucleophilicity (the negative charge is spread in the sulphonate ion) will react at different speeds, as found. Such a mechanism therefore probably obtains. The exact nature of the intermediate is not known. For isopropenyl acetate (III) and



hydrogen chloride in acetic acid it might be one of the species (A—C). In the light of some other work,<sup>5</sup> (A) seems most likely, but this is rather unattractive for catalysis by (say) perchloric acid, though the intermediate need not have the same form for every catalyst.

Step (1) in these reactions is actually very similar to step (−2). The latter involves attack by catalyst on acetic anhydride, a molecule closely related structurally to isopropenyl acetate (III). If step (−2) proceeds analogously to step (1), as seems possible, a rapid protonation equilibrium at one carbonyl group being followed by a slow nucleophilic attack by the anion at the other, then its rate with hydrogen chloride may be greater than that with toluene-*p*-sulphonic acid and perhaps even comparable with that for perchloric acid. Since the rates of step (+2) for hydrogen chloride and toluene-*p*-sulphonic acid may be much the same as each other, and much less than for perchloric acid, the very different positions for equilibrium (2) found with the different catalysts are seen to be compatible with the other data.

*Experimental.—Materials.* The acetates (I) and (II) were prepared as described by Hagermeyer and Hull.<sup>8</sup> The former had b. p. 65°/10 mm., and the latter 96°/5 mm. Acetic acid and the catalysts were previous samples.<sup>1</sup> Cyclohexanone and acetophenone were purified commercial materials.

*Reaction stoichiometry.* Reaction mixtures (with any catalyst) which had been left for more than ten half-lives, always had u.v. light absorptions which corresponded extremely closely to the absorptions of synthetic product mixtures. Acylation of acetic acid is thus doubtless complete and essentially free from side-reactions, under the conditions used.

*Kinetic procedures.* These were based on the methods of Part III. Reactants and products, with both acetates (I) and (II), had sufficiently different light absorptions to permit accurate estimation of the rate of product formation. All experiments were at 40°.

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<sup>8</sup> Hagermeyer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.