354. *Acylation. Part III.* Acid-catalysed Acetylation by Isopropenyl Acetate.*

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Acetylation of acetic acid by isopropenyl acetate yields acetone and acetic anhydride in high yield. The reaction is catalysed by strong acids. Its mechanism, when the catalyst is hydrogen chloride, hydrogen bromide, perchloric acid, sulphuric acid, toluene-*p*-sulphonic acid, methanesulphonic acid, or sulphoacetic acid has been examined in a kinetic and tracer study. A suggestion that keten is an intermediate in such catalysed acetylations proves unfounded.

In an excess of acetic acid, as solvent, a common two-stage mechanism is considered to operate with all the above catalysts (HX) (except sulphuric acid), namely:

$$CH_2{=}CMe{\cdot}OAc + HX \longrightarrow COMe_2 + XAc \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$XAc + AcOH \rightleftharpoons Ac_2O + HX \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

For the halogen acids the equilibrium (ii) lies far to the left, and for the other catalysts far to the right. The active acetylating agent is XAc. The velocity of step (i) is greater the greater the conventional acid strength of the catalyst.

Catalysis by sulphuric acid is complicated by its rapid, and quantitative, reaction with isopropenyl acetate to give a sulphonic acid (probably acetonesulphonic acid). This product catalyses the further solvolysis of isopropenyl acetate, as do other sulphonic acids.

The finer details of steps (i) and (ii) are discussed.

The general similarity between the mechanisms of acid-catalysed acetylation by compounds such as isopropenyl acetate, and by anhydrides, is pointed out. Their close interrelation when the solvent is acetic acid is emphasised.

Isopropenyl esters (I; R = Me) and esters of similar structure may be used to acylate a wide variety of compounds.[1] Though studied from the preparative viewpoint, these

* Part II, *J.*, 1961, 5404.

[1] Hagermayer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.

reactions have not been analysed kinetically. We report now * a kinetic and tracer study of the acetylation of acetic acid by isopropenyl acetate (I; R = R′ = Me); the products

$$CH_2{:}CR{\cdot}O{\cdot}COR' + AcOH \longrightarrow CH_3{\cdot}COR + AcO{\cdot}COR'$$
(I)

are acetone and acetic anhydride. At ordinary temperatures the reaction is slow in the absence of catalysts but is catalysed by strong acids. We have examined the effects of a number of these.

Wasserman and Wharton have made a tracer study of the interaction of the reactive methoxyvinyl benzoate (I; R = OMe, R′ = Ph) with both oxygen-labelled benzoic acid [2] and aqueous hydrogen chloride.[3] Their results are discussed with ours below.

Experimental

Materials.—Isopropenyl acetate was kindly supplied by Distillers Company Limited. It was redistilled (b. p. 97°). The acetone content, determined by addition of an excess of hydroxylamine hydrochloride to an ethanolic solution, followed by back-titration against sodium hydroxide, was found to be very small (<2%).

Dry hydrogen chloride was prepared by addition of the concentrated aqueous acid to concentrated aqueous sulphuric acid, the gas being bubbled again through the latter acid. Aqueous hydrogen bromide, aqueous perchloric and sulphuric acid, and hydrated toluene-*p*-sulphonic acid and methanesulphonic acid were commercial " pure " samples and were used without further purification. A solution of sulphoacetic acid in anhydrous acetic acid was prepared [4] by addition of the calculated quantity of 96% sulphuric acid to a solution of acetic anhydride in acetic acid, this mixture being left for 5 days at 40°.

Dry acetic acid, pure acetic anhydride, and tritium-labelled hydrogen chloride were prepared as previously described.[5,6] The water content of the acetic acid was found by Karl Fischer tritation; it was usually <0·02M.

A stock solution of hydrogen chloride in acetic acid was prepared by bubbling in the dry gas. The chloride content was determined by titration. Apart from that of sulphoacetic acid (see above), the stock solutions of the other acids were made up by weight from concentrated aqueous acid. The amount of water added in this process was small.

Kinetic Arrangements.—The reaction was followed by determining the acetone formed after suitable times, as isopropenyl acetate became completely solvolysed in an excess of acetic acid. Initial substrate concentrations were usually in the range 0·2—1·0M. The catalyst concentration depended on the acid in question, but was always considerably less than that of isopropenyl acetate (see Tables). Low concentrations were used to minimise medium effects.

Reaction mixtures were made up in 25 ml. stoppered volumetric flasks, by mixing solvent with suitable volumes of stock solutions of the catalysts and were maintained at 40° in a thermostat bath. The reaction was initiated by the addition of an appropriate volume of isopropenyl acetate. Samples (1 ml.) were withdrawn and run into carbon tetrachloride to quench the reaction. These solutions were made up to 10 ml. to provide solutions with appropriate light absorption. The acetone concentration was determined spectrophotometrically, by measurement at 2760 Å. In no case did other reaction components interfere. The measurements were made with a Beckman spectrophotometer and quartz cells of 1 cm. path.

The reproducibility of the observed rate constants was always within 4% and was often better.

Stoicheiometry of the Reactions.—Light-absorption measurements indicated that acetone formation was always closely quantitative. Nevertheless, the formation of the product was checked, for two of the catalysts, by comparing the infrared spectrum of a reaction mixture left for more than ten half-lives, with that of a synthetic mixture containing the expected

* For a preliminary communication see *Chem. and Ind.*, 1960, 1444.

[2] Wasserman and Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 1411.
[3] Wasserman and Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 661.
[4] Murray and Kenyon, *J. Amer. Chem. Soc.*, 1940, **62**, 1230.
[5] Satchell, *J.*, 1960, 1752.
[6] Satchell, *J.*, 1960, 4388.

amounts of acetone and acetic anhydride. The pairs of spectra were, in each case, identical. Side reactions must therefore be negligible.

Reaction between Sulphuric Acid and Isopropenyl Acetate.—If sulphuric acid is added to a solution of isopropenyl acetate in anhydrous acetic acid at 40°, and the mixture tested for free sulphate at frequent intervals (by boiling a sample with water and then adding barium chloride solution) very little can be detected after *ca.* 30 sec. This suggests, not only that sulphuric acid may be combining with the isopropenyl acetate, but also that it produces a sulphonic acid rather than a sulphate. The resulting acid solution is stable and, in fact, catalyses the solvolysis of any excess of isopropenyl acetate in a manner characteristic for sulphonic and other very strong acids (see Discussion).

An attempt was made to isolate the products of the reaction between sulphuric acid and isopropenyl acetate as follows. To a two-phase system of n-heptane (100 ml.) and 96% sulphuric acid (5 ml.) was added isopropenyl acetate (15 ml.), which dissolved in the heptane layer. The mixture was cooled. Reaction occurred at the interface, the sulphuric acid was consumed, and a yellow oil was formed. This oil was separated and washed with heptane. Samples of the oil were taken (*a*) as a catalyst for the reaction of isopropenyl acetate with acetic acid, (*b*) for addition to water and subsequent titration against sodium hydroxide with phenolphthalein and Methyl Orange as indicators, (*c*) for preparation of the benzylisothiouronium derivative [the recrystallised product of this reaction had m. p. 141° (Found: C, 49·2; H, 6·4; N, 11·9; S, 13·45%)], and (*d*) for preparation of the barium salt by the addition of water and then of barium carbonate. The barium derivative from (*d*) was appreciably soluble and therefore, after filtration, the solution was evaporated to dryness. A final drying, in a vacuum at 120°, led to an analysis: Ba, 38·0; C, 15·2; H, 2·2; S, 9·3%.

Discussion of these experiments is deferred.

Experiments with Tritiated Media.—Isopropenyl acetate was decomposed at 40° in acetic acid containing tritium-labelled hydrogen chloride (0·5M) of known activity. After a time interval a sample of the fully reacted mixture was added to water, and acetate was precipitated as silver acetate by addition of aqueous silver nitrate to the neutralised solution (the conditions of neutralisation were such that any loss of carbon-bound activity by exchange must have been negligible [7]). The silver acetate was recovered, washed, and dried. A weighed amount was then shaken with concentrated aqueous hydrogen chloride (this process was independently shown to produce at least 93% conversion into silver chloride and acetic acid). The mixture was diluted and centrifuged. A sample of the supernatant liquid was assayed for radioactivity by a scintillation technique. Corrections necessary for the quenching action of the components of the sample were found to be small.

A similar experiment was performed with tritium-labelled sulphuric acid (0·18M) as catalyst.

In both experiments the period allowed before sampling was long compared with that necessary for complete reaction of the isopropenyl acetate. During this period the acetic anhydride produced may undergo acid-catalysed exchange with the medium, and the medium itself may accumulate carbon-bound activity, though the latter process, at least is likely to be slow under the experimental conditions used.[7] To estimate the tritium incorporated in this period, as distinct from that incorporated during the solvolysis of the isopropenyl acetate, parallel experiments were performed with equivalent concentrations of acetic anhydride, instead of isopropenyl acetate, using similar time intervals. The results are given and discussed below.

Results and Discussion

For all catalysts the reaction between isopropenyl acetate and acetic acid was studied by decomposing a small amount of the former in the latter as solvent. Throughout the Discussion it must be borne in mind that in acetic acid strong acids, though they may be ionised to some degree, are little dissociated.[8]

Catalysis by Hydrogen Chloride.—(i) *Kinetic form of reaction.* The rate of acetone production (and thus the rate of disappearance of isopropenyl acetate) was not found to obey any simple kinetic law. However, since the acetate is known to react with halogen

[7] Bok and Geib, *Z. phys. Chem.*, 1938, *A*, **183**, 353.
[8] Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

acids to give acetone and acetyl halides,[1] and acetyl halides are known to engage in a rapid equilibrium with acetic acid,[5] the following mechanism was considered:

$$CH_2{:}CMe{\cdot}OAc + HCl \xrightarrow{k_1} COMe_2 + AcCl \quad (1)$$

$$AcCl + AcOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ac_2O + HCl \quad (\text{Fast}) \quad (2)$$

The equilibrium (2) is known to lie well on the left-hand side, so that once the reaction has begun, little free hydrogen chloride will exist in the system.

If A = acetone concentration at time t, B = isopropenyl acetate concentration at time t, B_0 = initial isopropenyl acetate concentration, C = stoicheiometric hydrogen chloride concentration, and square brackets represent concentration generally, then

$$dA/dt = k_1B[HCl], \quad (3)$$

and

$$d[HCl]/dt = k_2[AcCl][AcOH] - k_1B[HCl] - k_{-2}[Ac_2O][HCl],$$

where k_1, k_2, and k_{-2} are rate constants for steps (1) and (2). At any time t,

$$B_0 = B + A$$

and

$$C = [HCl] + [AcCl].$$

We now make the approximation that $[Ac_2O] \approx A$; in practice the quantities differ by $C - [HCl] \approx C$, but this error becomes less and less significant as the reaction proceeds; more rigorous equations may be developed by using the excellent approximation $[Ac_2O] \approx A - C$, but the analysis is, in fact, rather insensitive to the change so that this refinement is unnecessary. By our approximation we have:

$$d[HCl]/dt = k_2(C - [HCl])[AcOH] - k_1(B_0 - A)[HCl] - k_{-2}A[HCl].$$

Applying the steady-state treatment, and thus assuming that $d[HCl]/dt = 0$, we find

$$[HCl] = k_2[AcOH]C/\{k_1(B_0 - A) + k_2[AcOH] + k_{-2}A\}. \quad (4)$$

From (3) and (4) we derive

$$dA/dt = k_1(B_0 - A)k_2[AcOH]C/\{k_1(B_0 - A) + k_2[AcOH] + k_{-2}A\}.$$

Integration and the boundary condition that $A = 0$ at $t = 0$ show that

$$\ln \frac{B_0}{B_0 - A} - \frac{KB_0}{1 + KB_0}(1 - k_1/k_{-2})\frac{A}{B_0} = k_1Ct/(1 + KB_0), \quad (5)$$

or

$$\log \frac{B_0}{B_0 - A} - \frac{KB_0}{2{\cdot}3(1 + KB_0)}(1 - k_1/k_{-2})\frac{A}{B_0} = k_1Ct/2{\cdot}3(1 + KB_0),$$

where $K = k_{-2}/k_2[AcOH]$.

As noted, in the present system, equilibrium (2) is known to lie well on the left-hand side. Thus K will be large and $KB_0 \gg 1$. Hence

$$\log B_0/(B_0 - A) - (1 - k_1/k_{-2})A/2{\cdot}3B_0 = k_1Ct/2{\cdot}3KB_0. \quad (6)$$

If the proposed mechanism is of the correct type, then, with $P = (1 - k_1/k_{-2})/2{\cdot}3$ and $Q = k_1C/2{\cdot}3KB_0$, a plot of $(1/t)\log B_0/(B_0 - A)$ against A/B_0t should, for a given set of initial concentrations (B_0 and C), be linear with a positive slope P and an intercept Q. Such plots are indeed excellent straight lines (Fig. 1). The results for a variety of values of B_0 and C are given in Table 1. It may be seen that both P and QB_0/C also remain closely constant.

A further test of the scheme is available. If acetic anhydride is added initially, this

will affect equilibrium (2), and thus the course of the reaction, in a predictable way. If the initial anhydride concentration is d, then equation (5) becomes

$$\ln \frac{B_0}{B_0 - A} - \frac{KB_0}{1 + K(B_0 + d)} (1 - k_1/k_{-2}) \frac{A}{B_0} = k_1 Ct/[1 + K(B_0 + d)]; \qquad (7)$$

and equation (6) becomes

$$\log \frac{B_0}{B_0 - A} - \frac{B_0}{2{\cdot}3(B_0 + d)} (1 - k_1/k_{-2}) \frac{A}{B_0} = k_1 Ct/2{\cdot}3K(B_0 + d). \qquad (8)$$

Two runs at the same values of B_0 and C, but in one case with an initial anhydride concentration d, should provide plots with slopes in the ratio $B_0/(B_0 + d)$ [cf. equations (6) and (8)]. The values in Table 2 show this to be so.

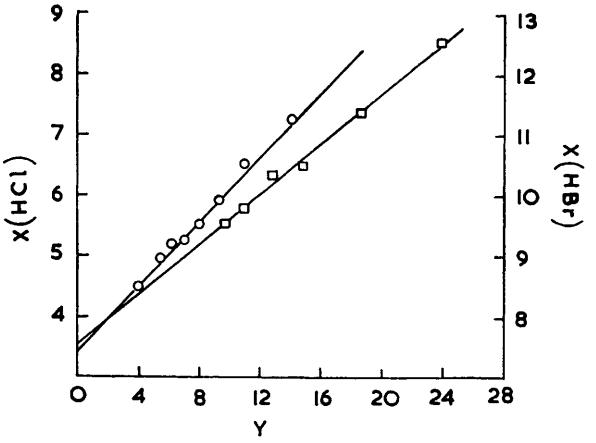


FIG. 1. Plots of (X) $(10^3/t)$ log $B_0/(B_0 - A)$ against (Y) $10^3A/B_0t$ (see equation 6) for catalysis by (○) hydrogen chloride and (□) hydrogen bromide.

Two final matters concern the initial addition of acetone, which should not affect the kinetics (and does not), and the removal of the last traces of water from the acetic acid solvent, which might otherwise affect the catalyst activity. The latter effect is very unlikely with the present catalyst, (*a*) because it will exist largely as acetyl

TABLE 1.

Values of P and Q obtained from plots of equation (6) for the hydrogen chloride-catalysed reaction at 40°.

B_0 = Initial isopropenyl acetate concentration; C = catalyst concentration. Concentrations are in moles/l. in all Tables.

B_0	C	P	10^2Q	QB_0/C	B_0	C	P	10^2Q	QB_0/C
0·720	0·0406	0·281	0·620	0·110	0·375	0·0300	0·300	0·900	0·112
0·718	0·0580	0·283	1·00	0·127	0·383	0·0302	0·252	1·13	0·140
0·718	0·0281	0·270	0·465	0·117	0·383	0·0126	0·273	0·343	0·104
0·718	0·0143	0·292	0·203	0·102	0·195	0·0110	0·273	0·600	0·106

TABLE 2.

The effect of added acetic anhydride on the constants P and Q for the hydrogen chloride- and hydrogen bromide-catalysed reactions

d = Initial acetic anhydride concentration; B_0 and C as in Table 1.

	B_0	C	d	$PB_0/(B_0 + d)$	$QB_0/(B_0 + d)$	P	QB_0/C
HCl catalysis	0·383	0·0130	0·172	0·166	0·00243	0·247	0·104
HBr catalysis	0·391	0·0020	0·451	0·100	7·2	0·215	3·01

chloride and (*b*) because small additions of water have little effect on the acidity of hydrogen chloride–acetic acid mixtures.[9] However, the solvent may easily be rendered closely

[9] Smith and Elliott, *J. Amer. Chem. Soc.*, 1953, **75**, 3566.

anhydrous by adding to it an appropriate amount of acetic anhydride and leaving the mixture for a suitable interval in the presence of the catalyst. If this is done, no change in the rate of solvolysis of isopropenyl acetate is found.

With these points in mind, it seems that there are good grounds for thinking that the proposed kinetic analysis is along the right lines. However, the particular mechanism suggested in equations (1) and (2) is not the only one that may lead to the kinetic form found: it may be elaborated to include the intermediacy of keten, in two ways:

(*a*) $CH_2{:}CMe{\cdot}OAc + HCl \longrightarrow COMe_2 + CH_2{:}CO + HCl$

$CH_2{:}CO + HCl \longrightarrow AcCl$ Fast

$AcCl + AcOH \rightleftharpoons Ac_2O + HCl$ Fast

or (*b*) $CH_2{:}CMe{\cdot}OAc + HCl \longrightarrow COMe_2 + CH_2{:}CO + HCl$

$CH_2{:}CO + AcOH \longrightarrow Ac_2O$ Fast

$Ac_2O + HCl \rightleftharpoons AcCl + AcOH$ Fast

Hagermayer and Hull, in their review [1] of acid-catalysed acylations by isopropenyl acetate, suggest the intermediate formation of keten, and its action as the active acylating agent [*e.g.*, scheme (*b*)]. The possibility of keten formation in the present system may be tested by carrying out the reaction in isotopically labelled acid. Such experiments are described below.

(ii) *Experiments in a labelled solvent system.* If isopropenyl acetate is decomposed in a tritium-labelled solvent, then, since mechanism (1) and (2) will provide only carbon-labelled acetone whereas schemes involving keten [*e.g.*, (*a*) and (*b*)] will produce also carbon-labelled acetic acid and anhydride, a distinction is possible.

$AcOT + HCl \rightleftharpoons AcOH + TCl$

Then either $CH_2{:}CMe{\cdot}OAc + TCl \longrightarrow CH_2T{\cdot}COMe + AcCl$

$AcCl + AcOT \longrightarrow Ac_2O + TCl$

or $CH_2{:}CMe{\cdot}OAc + TCl \longrightarrow CH_2{:}CO + CH_2T{\cdot}COMe + HCl$

$CH_2{:}CO + AcOT \longrightarrow CH_2T{\cdot}CO{\cdot}OAc$

$CH_2T{\cdot}CO{\cdot}OAc + TCl \rightleftharpoons \begin{cases} AcOT + CH_2T{\cdot}COCl \\ CH_2T{\cdot}CO_2T + AcCl \end{cases}$

In an experiment of this design (see Experimental) the activity was introduced as tritium-labelled hydrogen chloride, the hydrogen atoms of which undergo rapid exchange with the carboxylic hydrogen atoms of acetic acid.[10] After complete reaction of the isopropenyl acetate, a sample of the resulting acetyl groups was assayed for tritium, by procedures not conducive to loss of carbon-bound activity by exchange. Negligible tritium had found its way on to carbon. Consideration of the observed counts, the possible errors, and an isotope effect as large as 10 (which is unlikely [11]) for the step which incorporates the label leads to the conclusion that less than 2% (if any) of the reaction can proceed *via* keten. Indeed the very small activity incorporated during the control run with acetic anhydride (see Experimental) was greater than that incorporated during the ester decomposition.

We conclude that the mechanism outlined in equations (1) and (2) is very probably correct. Discussion of its finer details is deferred.

Catalysis by Hydrogen Bromide.—The nature of the experiments and the observed kinetic form of the reaction with this catalyst were similar to those described above for hydrogen chloride. The same rate equations proved satisfactory, though the experimental

[10] Gold and Satchell, *Quart. Rev.*, 1955, **9**, 51.
[11] Coe and Gold, *J.*, 1960, 4571.

quantities P and QB_0/C are of different magnitude. The results are given in Tables 2 and 3. The symbolism is as for hydrogen chloride catalysis. P and QB_0/C are, if anything, more

TABLE 3.

Values of P and Q obtained from plots of equation (6) for the hydrogen bromide-catalysed reaction at 40°.

B_0 and C as in Table 1.

B_0	C	P	10^3Q	QB_0/C	B_0	C	P	10^3Q	QB_0/C
0·407	0·00209	0·195	15·1	2·93	0·427 *	0·00020	0·203	1·20	2·64
0·405 *	0·00208	0·196	13·9	2·74	0·782	0·00200	0·200	7·50	2·92
0·417	0·00107	0·206	7·55	2·94	0·392	0·00398	0·207	28·0	2·76
0·422	0·00063	0·210	4·03	2·72	0·210	0·00213	0·200	30·0	2·96

* Reactions under anhydrous conditions.

TABLE 4.

Values of k_1/k_{-2} and k_2 for the hydrogen chloride- and hydrogen bromide-catalysed reactions at 40°.

Catalyst	P (average)	QB_0/C (average)	k_1/k_{-2}	k_2 (mole^{-1} min.$^{-1}$)
HCl	0·278	0·115	0·361	0·0457
HBr	0.202	2·79	0·536	0·750

nearly constant in the present case. A typical plot for hydrogen bromide catalysis is given in Fig. 1. That $P = (1 - k_1/k_{-2})/2{\cdot}3$, and $Q = k_1k_2[\mathrm{AcOH}]C/2{\cdot}3k_{-2}B_0$, allows k_1/k_{-2} and k_2 to be calculated. This has been done for average values of P and QB_0/C. The results are in Table 4. It may be seen (*a*) that acetyl bromide attacks acetic acid *ca.* 16 times faster than does acetyl chloride (this value is very reasonable in view of similar values for attack on water and on β-naphthol [5]), and (*b*) that the rate constants for attack by the catalyst on acetic anhydride and isopropenyl acetate are similar ($k_1/k_{-2} = 0{\cdot}3$—$0{\cdot}5$). We shall return to this point below.

Catalysis by Perchloric, Toluene-p-*sulphonic, Methanesulphonic, and Sulphoacetic Acid.*—The general kinetic pattern with all these acids is the same. The rate of acetone formation is of the first-order in both isopropenyl acetate and catalyst (stoicheiometric concentration). The rate is also essentially independent of the acetic anhydride concentration. If the catalyst is written as HX, the mechanism given in equations (9) and (10), which is similar to that proposed for hydrogen halide-catalysis but has the equilibrium lying well on the right-hand side, rather than on the left-hand side, is satisfactory for all these acids. [In view of the work with hydrogen chloride (see above) and sulphuric acid (see below) it is assumed that keten does not intervene.]

$$CH_2{:}CMe{\cdot}OAc + HX \xrightarrow{k_1} COMe_2 + AcX \qquad (9)$$

$$AcX + AcOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ac_2O + HX \qquad \text{(Fast)} \quad (10)$$

$AcX = AcClO_4$, $Ac{\cdot}SO_3Me$ $Ac{\cdot}SO_3{\cdot}C_6H_4Me$, or $Ac{\cdot}SO_3{\cdot}CH_2CO_2H$.

The species AcX (the acetyl derivatives of the catalysts) are, of course, the mixed anhydrides of acetic acid with HX. Acetyl perchlorate is known to be a very active species, and some previous evidence indicates [5] that for it the equilibrium (10) is achieved rapidly and lies well on the right-hand side. There is no reason to think such a circumstance unlikely for the other catalysts also. In such cases K ($=k_{-2}/k_2[\mathrm{AcOH}]$) will be small and equation (5) reduces to:

$$\log [B_0/(B_0 - A)] = k_1Ct/2{\cdot}3. \qquad (11)$$

This equation (11) predicts the observed first-order loss of substrate, the dependence on

stoicheiometric acid concentration, and the lack of dependence on acetic anhydride concentration. Results for the various catalysts are in Tables 5—8. Their further discussion is deferred. Typical first-order plots are given in Fig. 2. They were unaffected by using rigorously dried solvent.

TABLE 5.

Results for perchloric acid catalysis at 40°.

Initial isopropenyl acetate concentration 0·375—0·417M; C = Catalyst concentration; d = added acetic anhydride concentration; k_1 = second-order rate constant.

10^4C	11·9	6·46	3·38	2·02	3·85
d	—	—	—	—	0·40
k_1 (l. mole^{-1} min.$^{-1}$)	46·5	46·1	49·1	48·7	56·1

TABLE 6.

Results for toluene-*p*-sulphonic acid catalysis at 40°.

Initial isopropenyl acetate *ca.* 0·4M; C, d, and k_1 as in Table 5.

10^3C	1·65	4·42	8·09	8·63	16·5	3·30
d	—	—	—	—	—	0·40
k_1	1·76	1·73	1·66	1·62	1·71	1·67

TABLE 7.

Results for methanesulphonic and sulphoacetic acid catalysis at 40°.

Initial isopropenyl acetate concentration *ca.* 0·4M; C and k_1 as in Table 5.

	$Me{\cdot}SO_3H$			$HO_3S{\cdot}CH_2{\cdot}CO_2H$		
10^3C	2·64	5·16	9·87	2·55	4·66	6·70
k_1	1·17	1·14	1·10	6·40	6·12	6·64

TABLE 8.

Average values of k_1 for the different catalysts.

Catalyst	$HClO_4$	$C_6H_4Me{\cdot}SO_3H$	$Me{\cdot}SO_3H$	$HO_3S{\cdot}CH_2{\cdot}CO_2H$	H_2SO_4
k_1 (l. mole^{-1} min.$^{-1}$)	47·3	1·70	1·14	6·39	5·92

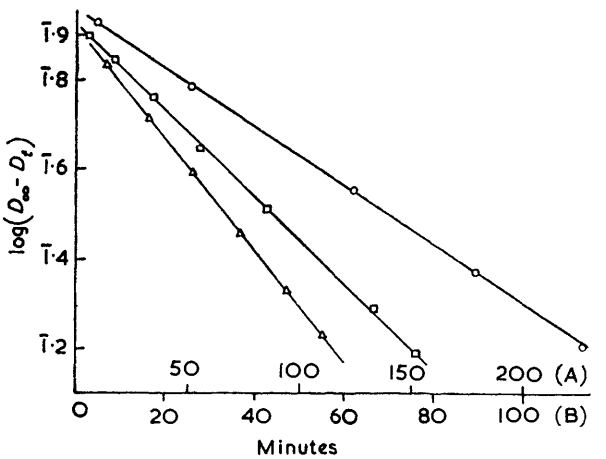


FIG. 2. Examples of first-order formation of acetone: Initial concn. of $CH_2{:}CMe{\cdot}OAc$ ~0·4M; D = optical density at 2760 Å. ○, *p*-$C_6H_4Me{\cdot}SO_3H$, $4{\cdot}42 \times 10^{-3}$M (scale A); □ $Me{\cdot}SO_3H$, $9{\cdot}87 \times 10^{-3}$M (scale A); Δ, $HO_3S{\cdot}CH_2{\cdot}CO_2H$, $4{\cdot}66 \times 10^{-3}$M (scale B).

Catalysts by Sulphuric Acid.—(i) *Kinetic form.* This is exactly as for the strong, monobasic acids discussed in the previous section. Moreover, the values of the observed rate constants, k_1, were close to those for sulphoacetic acid (see Tables 8 and 9). These

circumstances led us to suspect that sulphuric acid and isopropenyl acetate produced a monobasic sulphonic acid similar to sulphoacetic (or perhaps sulphoacetic acid itself) which then catalysed the further decomposition of isopropenyl acetate in the way characteristic for such acids.

(ii) *Reaction between sulphuric acid and isopropenyl acetate.* We tested the above hypothesis by analysing a solution of the ester and sulphuric acid in acetic acid for free sulphate at frequent intervals after mixing (see p. 1878). In concentration conditions usual for the kinetic experiments, little or no free sulphate remained after *ca.* 30 sec. This period is only a small fraction of the time of total solvolysis of isopropenyl acetate. Hence rapid reaction between the ester and sulphuric acid is probable.

TABLE 9.

Results for sulphuric acid catalysis at 40°.

B_0, C, d, and k_1 as in previous Tables.

B_0	10^3C	d	k_1	B_0	10^3C	d	k_1
0·383	1·23	—	5·94	0·379	4·82	—	5·93
0·376	2·40	—	5·75	0·720	4·62	—	5·72
0·379	2·40	—	5·92	0·379	4·82	0·415	6·10

It is not obvious what to expect as products of this reaction. Olefins usually produce hydrogen sulphates on reaction with sulphuric acid, not sulphonic acids.[12] However, hydrogen sulphates are subject to hydrolysis in aqueous solution, and our experimental test for free sulphate would most probably have induced some hydrolysis of any hydrogen sulphate present.[13] Since no free sulphate was found after a short while the product can hardly be a hydrogen sulphate. In view of its catalytic behaviour it is presumably a sulphonic acid. Sulphoacetic acid seems a possibility in view of the similarity of the rate data, but it is not easy to visualise its mode of formation.

In a preparative-scale reaction between sulphuric acid and isopropenyl acetate in heptane (see p. 1878), the product (obtained as a yellow oil) was found on titration in water to contain both a strongly and a weakly acidic centre. A benzylisothiouronium derivative proved to be that of acetic acid. The product might possibly be, therefore, a roughly equimolecular mixture of acetic acid and acetonemonosulphonic acid:

$$CH_2{:}CMe{\cdot}OAc + HSO_3^+\ OH^- \longrightarrow \left[\begin{array}{l} CH_2{-}SO_3H \\ \vdots \\ C \cdots O \cdots C{-}Me \\ Me \qquad O \end{array}\right]^+ OH^- \longrightarrow Ac{\cdot}CH_2{\cdot}SO_3H + AcOH$$

If this is assumed, then (*a*) the barium salt obtained from the product gives approximately the expected analysis and (*b*) the rate of solvolysis of isopropenyl acetate catalysed by a sample of the oil is close to the expected rate. We therefore suggest that sulphuric acid adds to the ester in a reaction involving an ionisation possibly characteristic of certain conventional sulphonation reactions.[14] It may be significant that an acid of the same elementary formula has been obtained from the reaction of isopropenyl acetate with sulphur trioxide in cold dioxan.[15]

The value of k_1 obtained with the sulphuric system suggests the formation of an acid catalyst slightly weaker (in the conventional sense) than sulphoacetic (see Tables 7 and 9). The proposed species satisfies this requirement for the only structural change is the substitution of methyl, with a $+I$ effect, for hydroxyl, with a $-I$ effect:

$$HO_3S{\cdot}CH_2{\cdot}CO{\cdot}OH \qquad HO_3S{\cdot}CH_2{\cdot}COMe.$$

[12] See, *e.g.*, Hickinbottom, " Reactions of Organic Compounds," Longmans, Green & Co., London, 1957.

[13] Shilov, Sabirova, and Gorshkov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **119**, 533.

[14] Gold and Satchell, *J.*, 1956, 1635.

[15] Terent'ev, Kost, Yurkevich, Khaskina, and Obreimova, *Vestnik Moskov Univ.*, 1953, **8**, [6], 121.

(iii) *Experiments in a labelled solvent system.* Sulphuric acid is perhaps the most commonly used catalyst in preparative work with isopropenyl acetate.[1] It is also a much stronger acid than hydrogen chloride, and therefore while the possible intervention of keten in the reaction scheme has been eliminated for the latter catalyst, it was desirable to test for it also with the former.

The experiments followed the pattern described for hydrogen chloride (see pp. 1878, 1881). With this acid a negligible amount of tritium becomes incorporated into acetic anhydride (or on to carbon of the solvent) during the experimental period. With sulphuric acid a small, though significant, exchange of this kind is obtained. Table 10 contains the

TABLE 10.

Experiments in labelled media.

Reactant	Time mixture was left at 40° (min.)	Count obtained in 100 sec.	Count per mole of AgOAc per 100 sec. (corr. for quenching)
Ester	10	801	$0{\cdot}74 \times 10^6$
Anhydride	10	2800	$2{\cdot}30 \times 10^6$
Ester	120	8860	$14{\cdot}4 \times 10^6$
Anhydride	110	16,000	$16{\cdot}0 \times 10^6$

(If all the reaction went *via* keten a count of 330×10^6 per mole of AgOAc would be expected, without allowance for an isotope effect.)

comparable results for the ester decomposition and the control run. Clearly very little tritium found its way on to carbon during the solvolysis of the ester. In the count/100 sec. expected if all the solvolysis went *via* keten (44,000) we have, as with hydrogen chloride, assumed that an isotope effect of 10 is involved for addition to the double bond. A notably smaller effect is likely,[11] and the expected count is therefore probably to be raised. In any event, after allowance for errors, less than 1%* (if any) of the ester solvolysis can proceed *via* keten.

(iv) *General conclusions.* Our general conclusions about sulphuric acid catalysis are at variance with previous expectations: the active catalyst is not sulphuric acid, but a sulphonic acid, probably acetonesulphonic; and the active acetylating agent is not keten, but the acetyl derivative of the sulphonic acid. The total mechanism for acetylation of acetic acid is:

$$CH_2{:}CMe{\cdot}OAc + H_2SO_4 \longrightarrow Ac{\cdot}CH_2{\cdot}SO_3H + AcOH \qquad \text{Fast}$$

$$CH_2{:}CMe{\cdot}OAc + Ac{\cdot}CH_2{\cdot}SO_3H \longrightarrow COMe_2 + AcO{\cdot}SO_2{\cdot}CH_2Ac$$

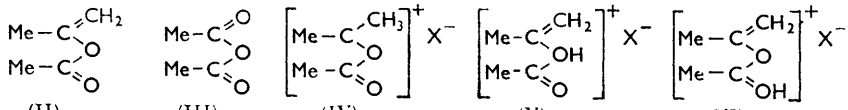
$$AcO{\cdot}SO_2{\cdot}CH_2Ac + AcOH \rightleftharpoons Ac_2O + Ac{\cdot}CH_2{\cdot}SO_3H \qquad \text{Fast}$$

Mechanistic Details and Related Work.—The essential steps in the mechanism of solvolysis for all the catalysts are those depicted in equations (9) and (10). The finer details of the three steps (1, 2, and −2) have so far been neglected. Step 2 requires little comment. It presumably involves nucleophilic attack by a carboxylic-oxygen atom of acetic acid on the carbonyl-carbon atom of AcX. To what extent this reaction is itself catalysed it is not possible to say. The process could be complicated in timing and geometry if dimeric acetic acid is involved (the solvent will be largely dimeric).

Steps 1 and −2 are basically similar, for the structure of isopropenyl acetate (II) is very like that of acetic anhydride (III). Step 1 is presumably initiated by the transference of a proton. However, the site of attachment is hardly certain. There are three possibilities (IV—VI). For methoxyvinyl benzoate (I; R = OMe, R′ = Ph) acid-catalysed hydrolysis in aqueous solution [3] seems to proceed by attachment, as in (IV),

* This figure involves the assumption that the rate of incorporation of activity into the product acetic anhydride, catalysed by (?) acetonesulphonic acid, is at least as rapid as such incorporation catalysed by sulphuric acid (the catalyst present in the control run). This is likely. It would have been better to use the product of the rapid isopropenyl acetate–sulphuric acid reaction as catalyst for the control run, but at that time we were not aware of the reaction.

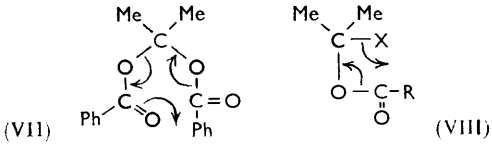
but the adjacent methoxyl group may be a reason for this. In the present case the adjacent group is only methyl. Nevertheless, the methylene group is certainly a possible site for proton addition.



(II) (III) (IV) (V) (VI)

Acid-catalysed reactions of ester-type compounds are attractively rationalised [16] by schemes involving initial proton attachment to their carbonyl groups rather than to their ethereal oxygen atoms [*e.g.*, (VI) rather than (V)]. In the present case, however, this mode of addition (VI) does not seem to lead easily to the products by simple electronic shifts.

While the ethereal oxygen atom may be the least basic of available sites, this is no reason to assume it is not the site which leads to further reaction.[16] In the present case addition as in (V) (the X^- ion being probably still weakly associated with the proton) with subsequent acyl fission seems a convenient stereochemical route to the products. However, with structure (VI) unlikely in the present instance, the weight of evidence probably favours addition as in (IV). As noted, this seems the case for methoxyvinyl benzoate in aqueous acid. Wasserman and Wharton [2] also consider, on the basis of tracer experiments, that the uncatalysed reaction of this compound with benzoic acid proceeds again by addition to the double bond (VII). They imply that prior addition of the catalyst to



(VII) (VIII)

the double bond is the likely first step in catalysed reactions also, the final product being formed by intramolecular rearrangement. For catalysis by HX this implies the intermediate (VIII).

For the analogous step −2, structures (IV) and (VI) become identical. Subsequent addition of X^- and electronic rearrangement (as in VIII) (or even the reverse of this order) are both possibilities for the completion of the process, but a scheme involving protonation as in (V) also remains possible.

While no decision can be made about the above details, yet a broad pattern of behaviour for vinyl esters and acetic anhydride, under acid catalysis, emerges from the present and previous work, namely: (*a*) In aqueous solutions of strong acid catalysts hydrolysis does not involve the acyl derivative of the catalyst,[17] but involves [18,3] either unimolecular decomposition of the conjugate acid of the substrate or nucleophilic attack on this species by water. (*b*) While aqueous solvolyses do not involve the acyl derivatives, nevertheless the present and previous work [5] shows that the solvolyses of, or acylation by, both types of compound in acetic and similar carboxylic acids do. They again behave similarly therefore.

The Usual Preparative Catalysts Used with Isopropenyl Acetate.—The most common of these are sulphuric acid, toluene-*p*-sulphonic acid, and a product (claimed as superior to sulphuric acid [1]) prepared by heating an excess (usually 2 mol.) of acetic anhydride with 1 mol. of sulphuric acid.[19] This product is probably acetylsulphoacetic acid [19,20] which we

[16] Bender, *Chem. Rev.*, 1960, **60**, 53.
[17] Gold and Hilton, *J.*, 1955, 838.
[18] Gold and Hilton, *J.*, 1955, 843; Bunton and Perry, *J.*, 1960, 3070; Koskikallio, *Acta Chem. Scand.*, 1960, **14**, 1343; Koskikallio, Pouli, and Whalley, *Canad. J. Chem.*, 1959, **37**, 1360.
[19] See, *e.g.*, Dommoni, U.S.P. 2,411,823; Schneider and Kraft, *Ber.*, 1922, **55**, 1892.
[20] Franchimont, *Rec. Trav. chim.*, 1888, **7**, 27.

conclude is the active acylating agent in catalysis by sulphoacetic acid (see p. 1882). Addition of this product is thus probably effectively addition of sulphoacetic acid as catalyst. It is shown above that catalysis by sulphuric acid is, in fact, catalysis by a sulphonic acid whose activity is only slightly lower than that of sulphoacetic acid. Claims for the special efficacy of acetylsulphoacetic acid are therefore difficult to understand. We consider the observed effects (which are largely changes in yield) are probably illusory or due to secondary causes.

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