358. *Acylation. Part VII.* The Kinetics and Mechanism of the Enol-acetylation of Acetophenone by Isopropenyl Acetate Catalysed by Toluene-*p*-sulphonic Acid.*

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Kinetic data on the enol-acetylation of acetophenone by isopropenyl acetate, catalysed by toluene-*p*-sulphonic acid, are reported and analysed. The acetophenone acted also as the solvent. It is concluded that the reaction involves three simultaneous equilibria:

$$Ph{\cdot}CO{\cdot}CH_3 + HX \rightleftharpoons CH_2{:}CPh{\cdot}OH + HX \quad (a)$$

$$CH_2{:}CMe{\cdot}OAc + HX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} COMe_2 + XAc \quad (b)$$

$$XAc + CH_2{:}CPh{\cdot}OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_2{:}CPh{\cdot}OAc + HX \quad (c)$$

where HX represents the catalyst. Of these equilibria, (*a*) is rapidly maintained in the systems discussed, the kinetic form being determined by (*b*) and (*c*). The values of k_1 and k_{-2} are very similar. The mechanism is compared with a similar scheme previously proposed for the acylation of acetic acid by isopropenyl acetate.[1]

Part III of this series [1] dealt with the kinetics and mechanism of the acetylation of acetic acid by isopropenyl acetate. This reaction, which produces acetic anhydride and acetone, is catalysed by strong acids (HX) and a number of these were studied. While useful for the production of anhydrides (particularly mixed anhydrides) isopropenyl acetate is especially valuable as a reagent for acylation of potential enols.[2] It has the advantages over other acylating agents of being generally applicable, of not attacking the olefinic bond of the enol species, and of undergoing little polymerisation. We report now a study of the acetylation of acetophenone by isopropenyl acetate catalysed by toluene-*p*-sulphonic acid. This acid is a catalyst often used in ordinary preparative work with isopropenyl acetate, and we conducted our experiments in an excess of acetophenone as solvent, thus using a formally non-hydroxylic medium, a circumstance which is also typical of preparative work.[2] (We emphasise the closeness to usual preparative conditions because we feel that organic chemists would be inclined to make more use of the conclusions of kinetic studies if these could be made to apply more closely to the systems which they actually use.) The product is α-acetoxystyrene, and the overall reaction is:

$$Ph{\cdot}CO{\cdot}CH_3 + CH_2{:}CMe{\cdot}OAc \overset{HX}{\rightleftharpoons} CH_2{:}CPh{\cdot}OAc + COMe_2$$

Since isopropenyl acetate is itself an enol-acetate, such reactions are in principle equilibria. In preparative practice they are driven to the right-hand side by distilling out the acetone as it is formed. In our kinetic experiments a similar result was achieved by using an excess of acetophenone.

Enol-acylation in general has been very little studied with a view to mechanistic elucidation. The work of Anderson *et al.*[3] on the enol-acetylation of steroids by acetic anhydride in toluene is the only other kinetic investigation: unfortunately, this study was very limited in extent, and the few results were consequently difficult to interpret.

* Part VI, preceding paper.

[1] Part III, Jeffery and Satchell, *J.*, 1962, 1876.
[2] Hagermayer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.
[3] Anderson, Garrett, Lincoln, Nathan, and Hogg, *J. Amer. Chem. Soc.*, 1954, **76**, 743.

Experimental

Materials. Commercially obtained acetophenone was dried over anhydrous calcium chloride for several days, filtered rapidly through glass wool, and fractionally distilled under reduced pressure from a dark flask. A fraction of b. p. 54°/2·5 mm., $n_D^{19\cdot3}$ $1\cdot5341_5$ was collected (lit., n_D^{19} 1·53418). The product was stored in a desiccator in a dark cupboard. A Karl Fischer estimation showed water in the product to be 0·01 ± 0·005M.

α-Acetoxystyrene was prepared by reaction of isopropenyl acetate with acetophenone toluene-*p*-sulphonic acid being used as catalyst, according to the method of Hagermayer and Hull.[2] After redistillation it had b. p. 89°/5 mm. Isopropenyl acetate was purified as previously described.[1] Toluene-*p*-sulphonic acid was obtained commercially as the monohydrate and was used as such (see below).

Kinetic Procedure.—Partly because the catalyst was added as the monohydrate it was thought desirable to use it in low concentrations. Since under these conditions the reaction proved slow at room temperature, to obtain convenient rates a high temperature (105·3°; oil thermostat-bath) was used. The mixtures were made from acetophenone (solvent), isopropenyl acetate, and toluene-*p*-sulphonic acid (monohydrate) in flasks (25 ml.) fitted with ground-glass stoppers in the form of cone and socket, the cone (rather than the socket) being part of the neck of the flask. The sockets were lightly greased to prevent the escape of acetone, this substance being the basis of the analytical method (see below). It was shown that acetone was not lost from the flasks during periods long compared with the duration of the kinetic experiments.

Since stock solutions of toluene-*p*-sulphonic acid in acetophenone become pale yellow on storage, the catalyst was weighed out afresh for each reaction mixture. The mixtures were made up at room temperature and then placed in the thermostat-bath where they quickly (<5 min.) acquired a temperature close to 105·3°. During the first 2 min. the stoppers were loosened occasionally to prevent pressure from being built up. At suitable intervals samples (1 or 2 ml.) were withdrawn for analysis.

Analytical Method.—To determine the acetone in the reaction mixture the following standard procedure was adopted. The sample (1 or 2 ml.) of reaction mixture was run into water (10 ml.) and shaken for 1 min., completely quenching the reaction, then cooled to 25° and centrifuged. The top layer (aqueous), contained most of the acetone (>85%), virtually all of the catalyst, and a small amount of acetophenone. (The fates of the other chemicals were unimportant, but these compounds probably remain in the acetophenone layer because their solubility in water is low.) After the two-phase system had reached 25° in a thermostat-bath, 5 ml. of the supernatant water layer were withdrawn and added to a 25-ml. conical flask containing a large excess of aqueous hydroxylamine hydrochloride also at 25°. After a convenient time the resulting solution was titrated against aqueous sodium hydroxide (added from a microburette) to Bromophenol Blue. The end-point was taken 8 min. after the original mixing of the solutions in the flask. The use of hydroxylamine hydrochloride for the estimation of ketones is a well-studied method.[4] Neither isopropenyl acetate nor α-acetoxystyrene interferes with it. The acetone content of the original sample was determined from a calibration curve constructed by use of synthetic mixtures of acetophenone and acetone in the same procedure. When no acetone is present a constant titre is obtained owing to slow reaction of the hydroxylamine with the acetophenone which dissolves in the water layer. The reproducibility of duplicate acetone analyses was ±6% at 0·1M and proportionately better at higher concentrations.

The reproducibility of the observed rate constants was ±2%.

Stoicheiometry.—A reaction on a preparative scale was performed as for the preparation of acetoxystyrene given above. The acetone distilled out, at 58°, from the boiling mixture as it was produced, and the volume collected corresponded within 5% of that expected for complete reaction. The yield of α-acetoxystyrene obtained from the mother-liquors by neutralisation, followed by fractional distillation under reduced pressure, was also nearly quantitative. Since under such preparative conditions the process goes essentially to completion, it must in general be subject to only very minor side-reactions. Under the kinetic conditions, as will be seen below, the reaction proceeds to an equilibrium position which, however, lies well on the product side.

[4] Kolthoff and Stenger, " Volumetric Analysis," Interscience Publ. Inc., New York, Vol. II, 1947.

Results and Discussion

Kinetic Form.—The reactions all showed rapid initial formation of a small (*ca.* 0·015M) amount of acetone (see Fig. 1). This was assumed to be due to the trace of water present in the acetophenone (the water added in the form of the monohydrate of the catalyst was negligible compared with that initially present in the solvent). To test whether this initial acetone formation could be due to water, a small amount of this substance was added before the substrate; the initial reaction, in fact, then increased. The increment in the number of moles of acetone produced was twice the number of moles of water added. Water is therefore probably rapidly acylated to acetic anhydride in the reaction mixtures. A trace of acetic anhydride is not likely to affect the subsequent kinetics, if only because of the similarity of its behaviour to that of isopropenyl acetate.[1]

After the small, initial, rapid reaction, subsequent formation of acetone was slow, and its rate declined until an equilibrium position was reached. The amount of substrate that had reacted was then 80—90%. The results of a typical run are in Fig. 1.

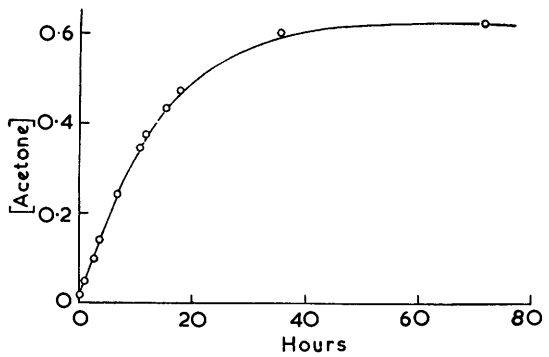

Fig. 1. Formation of acetone as a function of time.
Initial $[CH_2{:}CMe{\cdot}OAc] = 0{\cdot}769$M; [Catalyst] $= 0{\cdot}955 \times 10^{-3}$M.

The main reaction may be considered in two parts: (i) the setting-up of the keto-enol equilibrium for the acetophenone solvent, and (ii) the production of an acetylating agent and its acetylation of the enolic form of acetophenone.

(i) The exact mechanism of the setting-up and maintenance of the keto–enol equilibrium is not certain. Probably, however, the rapidity of the attainment of equilibrium increases in the presence of strong-acid catalysts (HX) while the equilibrium position remains unchanged. A representation of the equilibrium is therefore $Ph{\cdot}CO{\cdot}CH_3 + HX \rightleftharpoons CH_2{:}CPh{\cdot}OH + HX$. Further conjectures on this part of the reaction are deferred. (ii) The active acetylating agent is likely [1] to be acetyl toluene-*p*-sulphonate, produced by the reaction of isopropenyl acetate with the catalyst (HX):

$$CH_2{:}CMe{\cdot}OAc + HX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XAc + COMe_2 \quad \ldots\ldots\ldots (1)$$

Acetylation may then take place as follows:

$$XAc + CH_2{:}CPh{\cdot}OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_2{:}CPh{\cdot}OAc + HX \quad \ldots\ldots\ldots (2)$$

Remembering that the final equilibrium position lies fairly far on the acetone side (see above) we may, for a simple mathematical treatment (covering the early part of the reaction), neglect the back-reaction of acetone with acetylating agent. If the keto–enol equilibrium for the solvent is very rapidly maintained, the concentration of the enol form will be constant throughout the reaction. The system is then very similar to that for acid-catalysed acetylation of acetic acid.[1] There the corresponding reactions were:

$$CH_2{:}CMe{\cdot}OAc + HX \longrightarrow XAc + COMe_2$$

$$XAc + AcOH \rightleftharpoons Ac_2O + HX$$

The acetic acid, being the solvent, remained effectively constant in amount throughout the reaction.

If the present system is given a similar mathematical treatment to that accorded the acetic acid system, the relation between acetone concentration and time is given by: [1]

$$\log \frac{B_0}{B_0 - A} - \frac{KB_0}{2{\cdot}3(1 + KB_0)}\left(1 - \frac{k_1}{k_{-2}}\right)\frac{A}{B_0} = \frac{k_1 Ct}{2{\cdot}3(1 + KB_0)}, \quad (3)$$

where A = acetone concentration at time t, B_0 = initial isopropenyl acetate concentration, C = stoicheiometric catalyst concentration, and $K = k_{-2}/k_2[\mathrm{E}]$, where [E] is the enol concentration.

The experimental results are found to obey equation (1) if it is assumed that $k_1 \approx k_{-2}$ and that K is large. Under such conditions expression (1) reduces to:

$$\log \frac{B_0}{B_0 - A} = \frac{1}{2{\cdot}3}\frac{k_2[\mathrm{E}]Ct}{B_0}. \quad (4)$$

With the same assumptions, if α-acetoxystyrene is added initially in concentration d, the rate equation becomes:

$$\log \frac{B_0}{B_0 - A} = \frac{1}{2{\cdot}3} \cdot \frac{k_2[\mathrm{E}]Ct}{(B_0 + d)}. \quad (5)$$

As may be seen from the typical plot (Fig. 2), graphs of log $(B_0 - A)$ against t are straight lines for the first 1—2 half-lives of the substrate. If the initial slopes of such graphs are

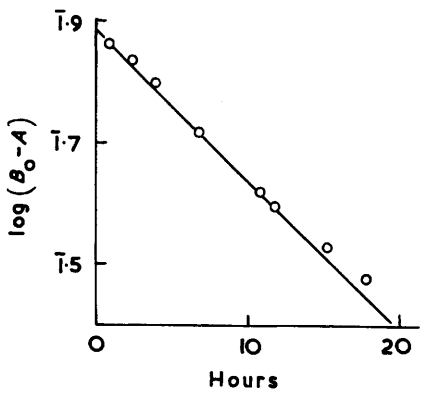

FIG. 2. Specimen plot of equation (3). Initial [CH_2:CMe·OAc] = 0·774M; [Catalyst] = 0·955 × 10^{-3}M.

taken and the factor $2{\cdot}3k_{obs}(B_0 + d)/C$ is calculated [where $k_{obs} = (1/t) \log B_0/(B_0 - A)$], then, as is seen from Table 1, the value of $2{\cdot}3k_{obs}(B_0 + d)/C$ (*i.e.*, $k_2[\mathrm{E}]$) is constant throughout the series of runs. This shows that the general equation (5) fits the results well. The assumptions of the treatment ($k_1 \approx k_{-2}$, and K large) are justified below. The curvature of the plots of log $(B_0 - A)$ against t at later stages is due to neglect of the back-reaction between XAc and acetone.

TABLE 1.

Enol-acetylation of acetophenone at 105·3°.

k_{obs}, $k_2[E]$, B_0, C, and d are defined under the treatment based on initial rates, and k_1 on p. 1908. Square brackets represent concentrations (M).

B_0	10^3C	d	10^2k_{obs} (l. mole^{-1} hr.$^{-1}$)	$k_2[E]$ (hr.$^{-1}$)	k_{-1} (l. mole^{-1} hr.$^{-1}$)	B_0	10^3C	d	10^2k_{obs} (l. mole^{-1} hr.$^{-1}$)	$k_2[E]$ (hr.$^{-1}$)	k_{-1} (l. mole^{-1} hr.$^{-1}$)
0·406	1·76	—	8·25	43·6	17·4	0·954	1·12	—	2·20	43·1	15·8
0·477	1·07	—	4·04	41·7	16·8	1·11	5·12	—	8·50	42·4	16·0
0·710	0·35	—	0·96	44·6	17·8	0·387	1·64	0·26	5·44	45·9	19·0
0·774	0·96	—	2·38	44·1	17·2						

The above simplified analysis emphasises the basic similarity of the present system to the previously studied acid-catalysed acetylation of acetic acid.[1] To obtain plots which are linear over more than 2 half-lives a more rigorous mathematical approach is necessary, as is next outlined.

Consider the equilibria (1) and (2), when the reverse step is *not* ignored. If B = isopropenyl acetate concentration at time t, S = α-acetoxystyrene, and the other symbols retain their previous meanings, then

$$\mathrm{d}A/\mathrm{d}t = k_1B[\mathrm{HX}] - k_{-1}A[\mathrm{AcX}], \tag{6}$$

and $$\mathrm{d}[\mathrm{HX}]/\mathrm{d}t = k_{-1}A[\mathrm{AcX}] + k_2[\mathrm{AcX}][\mathrm{E}] - k_1B[\mathrm{HX}] - k_{-2}[\mathrm{S}][\mathrm{HX}],$$

where k_1, k_{-1}, k_2, and k_{-2} are the appropriate rate constants for equilibria (1) and (2).

At any time t, $B_0 = B + A$, and $C = [\mathrm{HX}] + [\mathrm{AcX}]$. Also, under the experimental conditions, $A = [\mathrm{S}]$, so that we have:

$$\mathrm{d}[\mathrm{HX}]/\mathrm{d}t = k_{-1}A(C - [\mathrm{HX}]) + k_2(C - [\mathrm{HX}])[\mathrm{E}] - k_1(B_0 - A)[\mathrm{HX}] - k_{-2}A[\mathrm{HX}] \tag{7}$$

Using a steady-state assumption that $\mathrm{d}[\mathrm{HX}]/\mathrm{d}t = 0$ we find that

$$[\mathrm{HX}] = (k_{-1}A + k_2[\mathrm{E}])C/\{k_1(B_0 - A) + k_{-2}A + k_{-1}A + k_2[\mathrm{E}]\}. \tag{8}$$

Thus, from (6),

$$\frac{-(k_{-1} - k_1 + k_{-2})A - (k_1B_0 + k_2[\mathrm{E}])}{k_{-1}k_{-2}A^2 + k_1k_2A[\mathrm{E}] - k_1k_2B_0[\mathrm{E}]}.\mathrm{d}A = C.\mathrm{d}t. \tag{9}$$

On integration, with the boundary condition that at $t = 0$, $A = 0$, equation (9) becomes:

$$\theta_1 \ln \frac{k_1k_2[\mathrm{E}]B_0}{-k_1k_2A^2 - k_1k_2[\mathrm{E}]A + k_1k_2[\mathrm{E}]B_0} + \theta_2 \ln \frac{(\tau + A)A_\infty}{\tau(A_\infty - A)} = Ct, \tag{10}$$

where $$\theta_1 = (k_{-1} - k_1 + k_{-2})/2k_{-1}k_{-2},$$

$$\theta_2 = \frac{\left\{(k_1B_0 + k_2[\mathrm{E}]) - (k_{-1} - k_1 + k_{-2})\frac{k_1k_2[\mathrm{E}]}{2k_{-1}k_{-2}}\right\}}{2k_{-1}k_{-2}\left\{\frac{1}{4}\left(\frac{(k_1k_2[\mathrm{E}]}{k_{-1}k_{-2}}\right)^2 + \frac{k_1k_2[\mathrm{E}]B_0}{k_{-1}k_{-2}}\right\}^{\frac{1}{2}}},$$

$$\tau = \left\{\frac{1}{4}\left(\frac{k_1k_2[\mathrm{E}]}{k_{-1}k_{-2}}\right)^2 + \frac{k_1k_2[\mathrm{E}]B_0}{k_{-1}k_{-2}}\right\}^{\frac{1}{2}} + \frac{k_1k_2[\mathrm{E}]}{2k_{-1}k_{-2}}, \tag{11}$$

and $$A_\infty = \left\{\frac{1}{4}\left(\frac{k_1k_2[\mathrm{E}]}{k_{-1}k_{-2}}\right)^2 + \frac{k_1k_2[\mathrm{E}]B_0}{k_{-1}k_{-2}}\right\}^{\frac{1}{2}} - \frac{k_1k_2[\mathrm{E}]}{2k_{-1}k_{-2}}. \tag{12}$$

That the constant A_∞ is, in fact, the value of A at $t = \infty$ may be proved as follows. At $t = \infty$, $\mathrm{d}A/\mathrm{d}t = 0$, and then, from expression (9),

$$k_1k_2[\mathrm{E}]/k_{-1}k_{-2} = A_\infty^2/(B_0 - A_\infty). \tag{13}$$

Equation (12) results from solving expression (13) for A.

If the assumptions are now made that $k_1 \approx k_{-2}$ and that $k_{-2} \gg k_2\mathrm{E}$, then

$$k^2[\mathrm{E}]/k_{-1} = A_\infty^2/(B - A_\infty).$$

In practice, $A_\infty^2/(B_0 - A_\infty)$ is found to be *ca.* 3. Thus, if $k_{-2} \gg k_2[\mathrm{E}]$, then $k_1 \gg k_{-1}$. Under these conditions θ_1 is negligible compared with θ_2, and since it may be shown that the logarithmic terms in expression (10) are of comparable magnitude, we have:

$$2{\cdot}3\theta_2 \log \frac{(\tau + A)}{\tau} \cdot \frac{A_\infty}{(A_\infty - A)} = Ct.$$

By using the conditions that $k_1 = k_2$ and $k_1 \gg k_{-1}$ and an experimental value of A_∞, τ may be calculated. The final equation is:

$$\log \frac{(\tau + A)}{\tau} \cdot \frac{A_\infty}{(A_\infty - A)} = \frac{2}{2{\cdot}3} k_{-1} \left\{ \tfrac{1}{4} \left(\frac{k_2[\mathrm{E}]}{k_{-1}} \right)^2 + \frac{k_2[\mathrm{E}]B_0}{k_{-1}} \right\}^{\frac{1}{2}} \cdot \frac{Ct}{B_0} \quad (14)$$

It is gratifying that plots of $\log (A_\infty - A)/(\tau + A)$ against t are good straight lines for the entire course of the reaction. A typical graph is shown in Fig. 3.

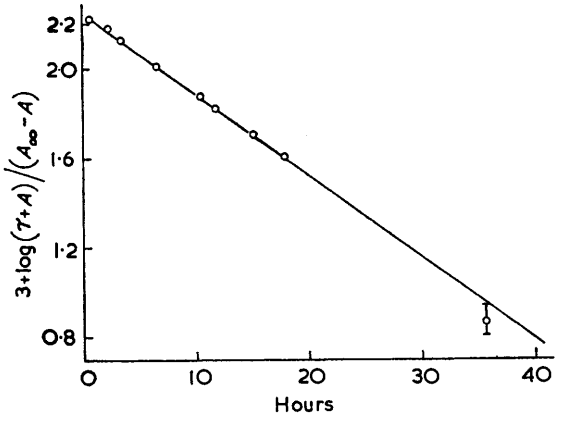

FIG. 3. Specimen plot of equation (14). Concns. as for Fig. 2.

When an initial concentration (d) of α-acetoxystyrene is added, equation (14) becomes

$$\log \left[\frac{(\tau' + A)}{\tau'} \cdot \frac{A_\infty}{(A_\infty - A)} \right] = \frac{2}{2{\cdot}3} k_{-1} \left\{ \tfrac{1}{4} \left(\frac{k_2[\mathrm{E}]}{k_{-1}} + d \right)^2 + \frac{k_2[\mathrm{E}]B_0}{k_{-1}} \right\}^{\frac{1}{2}} \cdot \frac{Ct}{(B_0 + d)}, \quad (15)$$

where

$$\tau' = \left\{ \tfrac{1}{4} \left(\frac{k_2[\mathrm{E}]}{k_{-1}} + d \right)^2 + \frac{k_2[\mathrm{E}]B_0}{k_{-1}} \right\}^{\frac{1}{2}} + \frac{k_2[\mathrm{E}] + dk_{-1}}{2k_{-1}}.$$

Values of k_{-1} calculated from the slopes of plots for different runs were reasonably constant (Table 1), as were values of $A_\infty^2/(B_0 - A_\infty)$ $(= k_2[\mathrm{E}]/k_{-1})$ for a series of runs with various catalyst and substrate concentrations (Table 2).

TABLE 2.

Equilibrium positions at 105° for different catalyst and substrate concentrations.

A_∞ = acetone concentration at $t = \infty$. Other symbols are as in Table 1.

B_0	10^3C	A_∞	$A_\infty^2/(B_0 - A_\infty)$
0·774	0·955	0·630	2·75
0·774	5·00	0·626	2·62
1·11	5·00	0·840	2·61

In summary it may be said that the more rigorous of the two mathematical treatments, when founded on the same numerical assumptions ($k_1 \approx k_{-2}$, $k_{-2} \gg k_2[\mathrm{E}]$), proves very satisfactory for representation of the experimental results. These assumptions, and the further postulate that keto–enol equilibration of acetophenone is rapid under the reaction conditions, will next be discussed.

Mechanistic Detail.—In the analyses above it was necessary to assume that the rate constants for attack by toluene-*p*-sulphonic acid on isopropenyl acetate and on α-acetoxystyrene are approximately equal, *i.e.*, $k_1 \approx k_{-2}$. As seen in Part III, the rates of attack of a strong acid, such as hydrogen bromide, on the structurally similar isopropenyl acetate and acetic anhydride, are probably of the same order. The suggestion was there made that

attack by the strong acid could take place either at the ethereal oxygen atom for both compounds, or at the methylene group for isopropenyl acetate and at the carbonyl group for the anhydride. In the present work we are concerned with α-acetoxystyrene, $CH_2{:}CPh{\cdot}OAc$, which is even more like isopropenyl acetate, $CH_2{:}CMe{\cdot}OAc$, than is acetic anhydride, $O{:}CMe{\cdot}OAc$. Indeed, the two compounds are essentially identical as regards either of the two positions of attack referred to above; the only difference is the substitution of Ph for Me on an adjacent carbon atom. One might, therefore, reasonably expect the value of k_1 to be very similar indeed to that of k_{-2}, no matter which site the catalyst attacks. These considerations are felt to justify our first assumption.

A second assumption is that the equilibrium (2) lies well on the left (*i.e.*, $k_{-2} \gg k_2[E]$). From general considerations this seems reasonable. However, in the work on the acetylation of acetic acid, by the same reagents, a condition arising in the mathematical examination was that the somewhat analogous equilibrium should lie well to the *right*.[1] Never-

$$XAc + O{=}CMe{\cdot}OH \rightleftharpoons O{:}CMe{\cdot}OAc + HX$$

theless, there is no necessary discrepancy here for, besides the fact that the two equilibria are only similar, and not identical in form, in the equilibrium involved in the present system the concentration of the enol species is extremely low, while in the acetic system the concentration of acetic acid was *ca.* 16M. The two equilibrium constants K' and K'', where

$$K' = [HX][CH_2{:}CMe{\cdot}OAc]/[XAc][CH_2{:}CPh{\cdot}OH]$$

and

$$K'' = [Ac_2O][HX]/[XAc][AcOH],$$

can therefore be of the same order while the respective ratios [HX]/[XAc] differ by powers of ten, at similar concentrations of anhydride and styrene. (The ketone : enol ratio in acetophenone has been determined by Gero;[5] he finds the concentration of the enol form in systems such as the present to be *ca.* 3×10^{-3}M.)

The final postulate necessary to our kinetic analysis is that keto–enol equilibration of acetophenone is fast compared with the acylation studied, so that a constant quantity of enol is present (see p. 1908). As a negative argument, we are aware of no reason why this should not be so. Also, the success of the treatment evokes confidence in its premises. We have no more positive argument than this, but nevertheless feel the scheme presented to be a most attractive possibility.

Concerning the mechanism of the enolisation of acetophenone, we have no definite information. In aqueous solution it involves proton addition by an acid and subsequent proton removal, from a different site, by a base.[6] Because of the prevalence of ion-pairs in solvents of low dielectric constant, there appear at least two possible variations in the present instance:

$$Me{\cdot}COPh + HX \rightleftharpoons [Me{\cdot}CPh{:}OH^+]X^- \rightleftharpoons CH_2{:}CPh{\cdot}OH + HX$$

$$2Me{\cdot}COPh + HX \rightleftharpoons Me{\cdot}COPh + [Me{\cdot}CPh{:}OH^+]X^- \rightleftharpoons CH_2{:}CPh{\cdot}OH + [Me{\cdot}CPh{:}OH^+]X^-, \text{ etc.}$$

In the former the associated anion effects proton removal itself. In the latter another molecule of the substrate species is involved.

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, October* 13*th*, 1961.]

[5] Gero, *J. Org. Chem.*, 1954, **19**, 1960.
[6] Swain and Rosenburg, *J. Amer. Chem. Soc.*, 1961, **83**, 2154.