The Kinetics of the Phenol–Styrene Reaction.

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Measurements of the rate of the acid-catalysed addition of styrene to phenol to give *o*- and *p*-1-phenylethylphenols in acetic acid solution at 25° show it to be of the second order. Quantitative theoretical treatment of the relationship between the rate constant and the initial phenol concentration gives good agreement between calculated and observed results. The second-order rate constant is proportional to the acetoxonium-ion concentration, and it is concluded that the acetoxonium ion is the effective catalyst.

The phenol–styrene reaction was first studied by Koenigs (*Ber.*, 1890, **23**, 3144; 1891, **24**, 3889) using acetic acid as solvent and sulphuric acid as catalyst. He obtained *p*-1-phenylethylphenol, a liquid isomer, and resinous products of higher molecular weight. Stoermer and Kippe (*Ber.*, 1903, **36**, 4012) assumed the liquid isomer to be *o*-1-phenylethylphenol. Pickard and Littlebury (*J.*, 1906, **89**, 469) resolved the compound isolated by Koenigs into its optical isomers by reaction with (—)-menthylcarbimide. The (+)- and the (—)-isomer both melted at 64°. McGreal and Niederl (*J. Amer. Chem. Soc.*, 1935, **57**, 2625) obtained the same compound by condensing 2-phenylethanol with phenol in the presence of zinc chloride and assumed that the alcohol lost water to form styrene which then reacted with phenol. Recently Frisch (*J. Org. Chem.*, 1950, **15**, 587) prepared a number of derivatives of *o*- and *p*-1-phenylethylphenol and Buu Hoï (*J. Org. Chem.*, 1952, 1952, **17**, 243) carried out several condensations closely related to the phenol–styrene reaction.

The overall reaction is summarised by the scheme : $\mathrm{PhOH} + \mathrm{CH_2{:}CHPh} \longrightarrow$ a mixture of *o*- and *p*-1-phenylethylphenol, but no reaction mechanism based on kinetic measurements has been suggested. Acetic acid was chosen as the solvent because, first it was known from Koenigs's work that the reaction proceeded in that medium at a measurable rate, and secondly there is considerable information available about the properties of acids dissolved in acetic acid; in particular Conant and Hall (*J. Amer. Chem. Soc.*, 1927, **49**, 3047, 3062) studied the strengths of different acids in acetic acid by both electrometric and indicator methods.

In preliminary experiments, sulphuric acid was used as catalyst but, as this was consumed during the reaction, perchloric acid was chosen. There seemed to be less possibility of side reactions between catalyst and reactants with this acid, and Conant and Hall (*loc. cit.*) and Kolthoff and Willman (*J. Amer. Chem. Soc.*, 1934, **56**, 1007) showed that perchloric acid is much more highly ionised than sulphuric acid in acetic acid. The use of a highly-ionised acid is advantageous as it reduces the number of catalytic species present to the solvated proton and the perchlorate ion. An appreciable quantity of un-ionised perchloric acid might also have a catalytic effect, but general acid catalysis is outside the scope of the present research.

Mackenzie and Winter (*Trans. Faraday Soc.*, 1948, **44**, 159) published results of kinetic studies on the acetic acid–acetic anhydride solvent system and included a useful survey of the properties of acids in acetic acid.

EXPERIMENTAL

Acetic acid, of " AnalaR " grade, was distilled to remove unsaturated materials, and dried by the method of Kendall and Gross (*J. Amer. Chem. Soc.*, 1921, **43**, 1428). Alternatively dehydration *in situ* by acetic anhydride proved satisfactory.

Perchloric acid, of " AnalaR " grade 60% aqueous solution, was standardised against " AnalaR " sodium carbonate.

" AnalaR " grade phenol was redistilled, the middle third being kept in a sealed container and exposed to the air for only a few seconds.

Styrene from the Dow Chemical Company, Koppers Co., and Boake Roberts & Co. showed no significant differences. It was freed from inhibitor and distilled under reduced pressure in an inert atmosphere before use.

All materials used in the analysis of reaction samples were " AnalaR " products except technical *cyclo*hexane which was sufficiently pure.

Methods.—For the preparation of the catalyst solution, a weighed quantity of aqueous perchloric acid was washed into a standard flask with acetic acid. Acetic acid was added, followed by the theoretical quantity of " AnalaR " acetic anhydride to react with all the water. The volume was made up with more acetic acid.

The heat of mixing of the perchloric acid and acetic anhydride was regarded as an indication of the rate of dehydration of the catalyst solution by acetic anhydride. Mackenzie and Winter (*loc. cit.*) showed by adding small amounts of water during the Thiele acetylation in acetic anhydride–acetic acid that dehydration is rapid. Dehydration was shown to be complete, by later work in which excess of acetic anhydride was added. The possibility of dehydration to give chlorine heptoxide and acetic acid was considered extremely improbable in view of the very large excess of acetic acid. The solution prepared as described above was stable, and a stock solution (500 ml.) was used for several series.

The catalyst solution was added from a burette to the graduated reaction flask, and solvent was added to the level of the lower of two marks which indicated the amounts of phenol and styrene to be added to give approximately the required initial concentrations. Acetic acid and a little acetic anhydride were added and the mixture kept for at least 4 hr. to ensure dehydration.

The liquid phenol was added from the distillation apparatus to bring the level to the second mark. The reaction mixture was kept for at least 12 hr. to allow the excess of acetic anhydride to react with phenol. The phenyl acetate thus produced would be in small concentration compared with the phenol and styrene, and presumably would not affect the rate constant.

After 12 hr., the reaction was started by adding styrene from a microburette up to the mark, and the first sample for analysis was taken immediately after the homogenising of the mixture. In most experiments, 100 ml. of reaction mixture were prepared.

Traces of water retarded the reaction considerably, and it was impossible to measure formal kinetics until this effect had been studied, and suppressed. Cryoscopic data were obtained on acetic acid–water and acetic acid–acetic anhydride; the cryoscope used was similar to that described by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1708).

A sample of nominally pure acetic acid, m. p. 16·65°, was prepared by the method of Kendall and Gross (*J. Amer. Chem. Soc.*, 1921, **43**, 1428), the product being fractionated and the first third discarded. The effect of the addition of water and acetic anhydride to acetic acid is shown in Fig. 1. In each case, the plot is linear as would be expected.

These cryoscopic measurements were made in conjunction with a series of determinations to establish the quantitative effect of water and acetic anhydride on the phenol–styrene reaction rate. In all cases the nominally pure fractionated acetic acid was used, and the results are illustrated in Fig. 2 where the second-order rate constants are plotted against the concentration of added water and acetic anhydride, severally. These measurements were made before the quantitative effect of phenol had been studied, but for all points plotted the initial phenol concentration was approximately molar.

Line *A* in Fig. 2 illustrates the sensitivity of the reaction to water. It will be seen that less than 0·1% of water present in the acetic acid is sufficient to reduce the rate constant by half its original value. Other factors being constant, this curve would be governed by the value of K_2 (see equation 2), although there are insufficient results to permit accurate calculation of this constant.

When excess of acetic anhydride was present, as in curve *B*, high and erratic values for the rate constant were obtained. In these experiments, the excess of acetic anhydride was added shortly before the start of reaction, and the erratic values for the rate constant are most probably due to simultaneous styrenation and acetylation of the phenol.

For curve *C* acetic anhydride and phenol were added, and styrene added 12 hr. later to commence the reaction. In these circumstances, the acetic anhydride would react with water in the acetic acid, but any acetylation would have ceased before the main reaction commenced. On addition of styrene, the reaction would proceed at a rate similar to that where pure acetic acid alone is used without any addition of anhydride as curve *C* confirms, thus rendering possible a satisfactory method for the *in situ* drying of acetic acid. If fractionated acetic acid was used for a rate determination, a slight excess of acetic anhydride would be added to account for any trace of adventitious water. If the acetic acid was known to have a small water content (calculated from its freezing-point by using Fig. 1) the required amount of acetic anhydride, preferably with a slight excess, would be added with the catalyst. These determinations led to the above standard procedure for initiating the reaction.

Fig. 1. *Cryoscopic measurements on acetic acid/water mixtures and acetic acid/acetic anhydride mixture.*

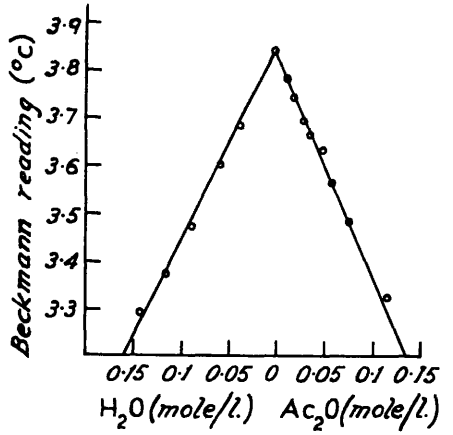
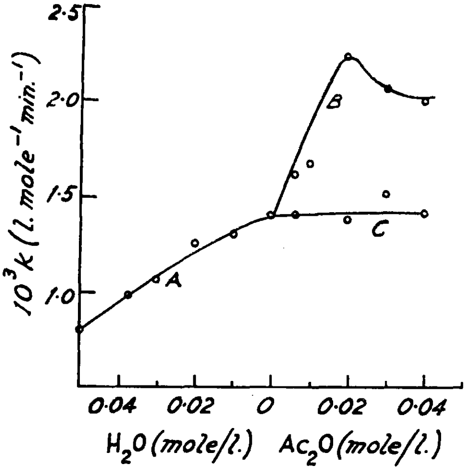


Fig. 2. *Quantitative effect of water and acetic anhydride on second-order rate constant.*



Traces of water in the phenol or styrene will not be removed but as the solubility of water in styrene is negligible the styrene never presented any difficulty. Batch variations in phenol, presumably due to traces of water, were observed despite purification.

Provided that the phenol was in considerable excess over the styrene, the further reaction of styrene with the initial products was suppressed, phenol and styrene reacting in equimolar proportions. The rate was determined by measuring the concentration of phenol at different times during reaction.

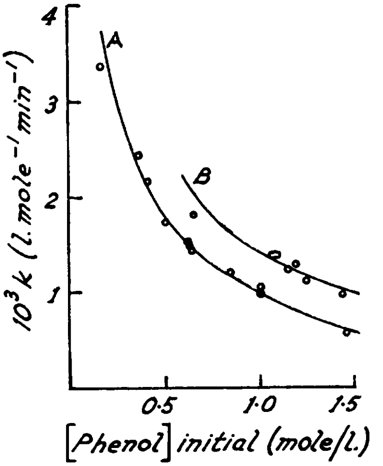
The styrene was added by volume; a density determination giving the initial concentration. Phenol was determined volumetrically by Koppeschaar's bromide–bromate method as modified by Redman, Weith, and Brook (*Ind. Eng. Chem.*, 1913, **5**, 389), a little carbon tetrachloride being added to dissolve the flocculent precipitate of tribromophenol which otherwise obscures the end point of the titration. The accuracy of the method was confirmed by using a standard solution of phenol in acetic acid.

Since both styrene and the products react with bromine, the phenol was extracted with water and determined in the extract. Acetic and perchloric acids extracted simultaneously are not brominated under these conditions.

The method of sampling and extraction was as follows :

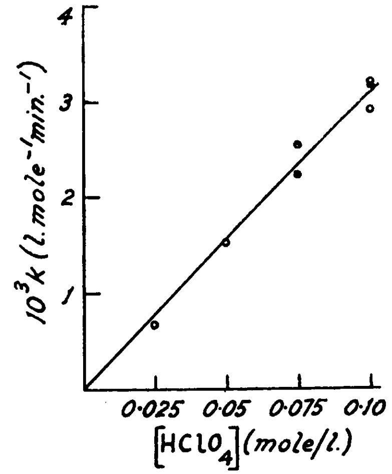
A sample (5 ml.) of reaction mixture was pipetted into a mixture of water (100 ml.) and *cyclo*hexane (75 ml.) in a 250-ml. tap-funnel, and the mixture stirred vigorously for about 10 min. The aqueous layer was removed and the *cyclo*hexane stirred with more water (100 ml.). The phenol in the aqueous extract was then determined. Analysis of mixtures of known composition showed the consistency of the results to be within 1%. The reaction temperature was maintained at 25 ± 0·1°.

FIG. 3. *Variation of second-order rate constant with initial phenol concentration.*



(A), G. & B. *phenol*; (B), B.D.H. *phenol*. Experimental points are shown. The curves are from theoretical calculations (see Discussion).

FIG. 4. *Variation of second-order rate constant with stoicheiometric catalyst concentration.*



Calculation of Results.—The results obeyed the second-order rate equation :

$$k = \frac{2{\cdot}303}{t(a - b)} \log_{10} \left\{\frac{b(a - x)}{a(b - x)}\right\}$$

where a = initial phenol concentration (mole/l.), b = initial styrene concentration (mole/l.), x = mole/l. of phenol consumed at time t (min.), and k = rate constant.

The styrene concentration $(b - x)$ at time t was calulated on the assumption that equimolar concentrations of styrene and phenol react as shown to be reasonable for the part of the reaction studied. In a trial determination, the results obeyed the equation, k being 0·00059 ± 0·00002 l. mole^{-1} min.$^{-1}$ over two-thirds of the reaction.

Dependence on Concentrations of Reagents.—The results of experiments in which the proportions of phenol and styrene were varied to confirm that k was independent of a and b are illustrated in Fig. 3 in which the observed rate constant is plotted against the initial phenol concentration for a range of styrene concentration 0·278—0·416M with the B.D.H. phenol and 0·125—0·424M with the G. and B. phenol. Despite all precautions, there was an inconsistency, which was identified with batch variations in the phenol, but it is concluded that a well-defined relationship exists between the rate constant and the initial phenol concentration although it is not possible to assign a second-order rate constant for the reaction in the ordinary way because of the variation with initial phenol concentration. The purity of the B.D.H. phenol being assumed, the rate constant of the phenol–styrene reaction at 25°, with 0·05M-perchloric acid as catalyst and 1·000M-initial phenol, is 0·00145 ± 0·00007 l. mole^{-1} min.$^{-1}$ which is the highest value obtained within the experimental error. The rate constant is independent of the initial styrene concentration over the ranges studied.

Dependence on Catalyst Concentration.—As shown in the previous section, the effect of varying the stoicheiometric catalyst concentration must be studied at constant initial phenol concentration. This was difficult owing to the method of preparation of the reaction mixture, but of the rate determinations carried out at various perchloric acid concentrations with the same batch of phenol, seven had initial phenol concentrations between 0·82M and 0·87M. Fig. 3 shows that the rate of change of observed rate constant with initial phenol concentration over this range is unlikely to introduce any significant error. Fig. 4 demonstrates the proportionality between rate constant and catalyst concentration up to a concentration of 0·1M-perchloric acid.

DISCUSSION

General Theory and Interpretation of Results.—Kolthoff has shown that the conductivity of perchloric acid in acetic acid solution is not greatly affected by the addition of small amounts of water, whereas the conductivity of sulphuric acid increases greatly when traces of water are added. He concluded that perchloric acid is largely ionised in acetic acid whereas sulphuric acid is not. Perchloric acid in acetic acid will therefore exist largely in the form of acetoxonium ions and perchlorate ions: $\mathrm{Me{\cdot}CO_2H + HClO_4 \rightleftharpoons Me{\cdot}CO_2H_2^+ + ClO_4^-}$. The most probable initial step in the mechanism of catalysis of the phenol–styrene reaction is the addition of a proton to a styrene molecule. However the protons formed by perchloric acid ionisation may be solvated by acetic acid, phenol, or water, and the rate of a given reaction will depend on the equilibria:

$$\mathrm{Me{\cdot}CO_2H_2^+ + PhOH \overset{K_1}{\rightleftharpoons} PhOH_2 + Me{\cdot}CO_2H} \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Me{\cdot}CO_2H_2^+ + H_2O \overset{K_2}{\rightleftharpoons} H_3O^+ + Me{\cdot}CO_2H} \quad . \quad . \quad . \quad . \quad (2)$$

where K_1 and K_2 are equilibrium constants.

The phenoxonium and oxonium ions may have an appreciable catalytic effect, but even if they have not, phenol or water will affect the concentration of the most strongly acidic species present, namely acetoxonium ion, and this explains qualitatively the relationship shown in Fig. 3. The following treatment gives a quantitative explanation of the variation of observed rate constant with initial phenol concentration. It is assumed that perchloric acid is completely ionised, that the reaction is of the first order with respect to hydrogen-ion concentration, and that constant ionic conditions prevail throughout a given reaction. The third assumption is justified since, although phenol is consumed, it is replaced by another phenol.

If k°, k_p°, and k_o° denote the catalytic constants for acetoxonium, phenoxonium and oxonium ion catalysis, respectively, and h, a^+, and o^+ are their respective concentrations, then the observed second-order rate constant k is given by $k = k^\circ h + k_p^\circ a^+ + k_o^\circ o^+$. By applying the mass law to equations (1) and (2), and treating the acetic acid concentration as constant, we obtain: $a^+ = K_1ah$ and $o^+ = K_2oh$.

Thus

$$k = h[k^\circ + k_p^\circ K_1a + k_o^\circ K_2o] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If C is the stoicheiometric concentration of perchloric acid and complete ionisation is assumed: $C = h + a^+ + o^+ = h[1 + K_1a + K_2o]$

so that

$$h = C/[1 + K_1a + K_2o] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substitution for h in (3) and setting $\gamma_1 = k_p^\circ/k^\circ$ and $\gamma_2 = k_o^\circ/k^\circ$ gives:

$$k = k^\circ C\left[\frac{1 + \gamma_1K_1a + \gamma_2K_2o}{1 + K_1a + K_2o}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If phenol is the only source of water (as in the present work), $o = c_1a$, where c_1 is the mole fraction of water in the phenol. Substituting for o in (5) and inverting, we obtain:

$$1/k = \frac{1}{k^\circ C} + \left[\frac{(K_1 + K_2c_1)a}{k^\circ C}\right]\left[\frac{1}{1 + (\gamma_1K_1 + \gamma_2K_2c_1)a}\right] \quad . \quad . \quad . \quad (6)$$

Now, if phenoxonium and oxonium catalysis are negligible compared with acetoxonium catalysis γ_1 and $\gamma_2 \approx 0$, and k°_p and $k^\circ_o \ll k^\circ$. Thus (6) reduces to the form $1/k = P + Qa$ where $P = 1/k^\circ C$ and $Q = (K_1 + K_2c_1)/k^\circ C$. The graph of $1/k$ against a should be a straight line of intercept P and gradient Q. P will not be subject to batch variation in the phenol, and from it k° can be calculated; Q depends on the water content of the phenol, but its limiting value, where $c_1 = 0$, gives K_1.

Fig. 5 shows the experimentally observed relationship between $1/k$ and a for two batches of phenol. The linearity demonstrates that phenoxonium and oxonium ion catalysis are not detectable under these conditions and that the effective catalyst is the acetoxonium ion. By using the values for P and Q given by Fig. 5, the curve for the relation between k and a shown in Fig. 3 is calculated.

From Fig. 5, $P = 90$ l.$^{-1}$ mole min. and $C = 0{\cdot}05$ mole l.$^{-1}$, from which $k^\circ = 1/PC = 0{\cdot}22$ l.^{2} mole^{-2} min.$^{-1}$.

If it is assumed that for the B.D.H. phenol $c_1 = 0$, then $Q = K_1/k^\circ C = K_1P$. The gradient Q for this batch is 614 min. whence $K_1 = 6{\cdot}8$ l. mole^{-1}.

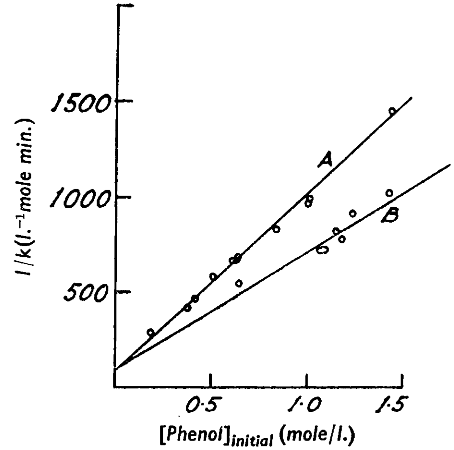


FIG. 5. *Variation of reciprocal rate constant with initial phenol concentration.*
(A), G. & B. *phenol*; (B), B.D.H. *phenol.*

From (6), it will be seen that the rate constant should be proportional to the stoicheiometric catalyst concentration, as demonstrated by Fig. 4. However, since $a^+ = K_1ah$, and $K_1 = 6{\cdot}8$ l. mole^{-1}, for a molar initial phenol concentration, only about an eighth of the perchloric acid is effective in catalysing the phenol–styrene reaction, even under anhydrous conditions.

In the above treatment it is assumed that the rate of reaction is of first order with respect to each catalytic species present. Since experimental results are in agreement with the theory derived from this assumption, and show k_p° and k_o° to be negligible, the observed rate constant is proportional to the acetoxonium-ion concentration, *i.e.*, $k = k^\circ h$. This being so the mechanism for the reaction suggested is as follows:

$$\mathrm{PhCH{:}CH_2 + Me{\cdot}CO_2H_2^+ \longrightarrow Ph\overset{+}{C}H{\cdot}CH_3 + CH_3{\cdot}CO_2H}$$

$$\mathrm{Ph\overset{+}{C}H{\cdot}CH_3 + C_6H_5{\cdot}OH \longrightarrow HO{\cdot}C_6H_4{\cdot}CHPh{\cdot}CH_3 + H^+}$$

The mechanism seems more likely than that suggested by Niederl and Natelson (*J. Amer. Chem. Soc.*, 1931, **53**, 272), which involved intermediate ether formation and rearrangement as a general mechanism for the addition of olefins to phenol:

$$\mathrm{RCH{:}CH_2 + H_2SO_4 \longrightarrow RCHMe{\cdot}O{\cdot}SO_3H}$$

$$\mathrm{RCHMe{\cdot}O{\cdot}SO_3H + C_6H_5{\cdot}OH \longrightarrow RCHMe{\cdot}O{\cdot}C_6H_5 + H_2SO_4}$$

$$\mathrm{RCHMe{\cdot}O{\cdot}C_6H_5 \longrightarrow RCHMe{\cdot}C_6H_4{\cdot}OH}$$

The authors used sulphuric acid as catalyst and isolated ethers from the reaction of olefins with phenol at 0°. At higher temperatures substitution occurred, although the ether was relatively stable once formed. Their experiments were not carried out in solution, and therefore the tendency for the sulphuric acid to add on to the olefin was greater than it would be in a solvent such as acetic acid. Even in acetic acid perchloric acid is stronger than sulphuric acid, and any intermediate would be more likely to exist in the form $[R{\cdot}\overset{+}{C}H{\cdot}CH_3]ClO_4^-$. The specific case of styrene was not considered by Niederl and Natelson, although 1-phenylethylphenol was obtained from 2-phenylethanol with phenol in the presence of zinc chloride.

The initial step of the mechanism suggested above is similar to that for the ionic polymerisation of styrene. Styrene polymerisation, like the styrene–phenol reaction, can be catalysed by Friedel–Crafts catalysts (Williams, *J.*, 1938, 246, 1046; 1940, 775; 1954, 357; see also Pepper, *Quart. Reviews*, 1954, **8**, 88), and the mechanism of similar ionic polymerisations has been the subject of considerable attention in recent years (Plesch "Cationic Polymerisation and Related Complexes," Heffer, Cambridge 1953, p. 70). In view of the present theory it is probable that the phenol–styrene reaction in acetic acid solution could be used to study under controlled ionic conditions the Friedel–Crafts catalysed polymerisation of styrene.

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