434. *The Mechanism of the Fries Rearrangement.*

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The rate of rearrangement of *o*-tolyl acetate in the presence of titanium tetrachloride in homogeneous nitrobenzene solution increased (*a*) with temperature, and (*b*) with the catalyst–ester molecular ratio up to a value of 2, after which, further increase in the ratio had scarcely any effect. The plot of mole % of ester against time for a 1 : 1 catalyst–ester ratio was very similar over a three-fold change in the volume of solvent. We conclude that the ester and catalyst combine immediately on mixing and that it is the further first-order reaction of this complex that is observed.

The products consisted almost entirely of the *para*-substituted hydroxy-ketone, and *o*-cresol. As the hydroxy-ketone was formed at a finite rate at zero time it must have come, in part at least, directly from the acetate–catalyst complex by an intramolecular migration. For the same reason the *o*-cresol must have arisen directly from a first-order scission of the complex; it subsequently reacted further to give, presumably, the hydroxy-ketone.

From the effect of temperature on the rate of disappearance of *o*-tolyl acetate, the activation energy for this reaction has been obtained.

Similar results were obtained with *o*-cresol and acetyl chloride in place of *o*-tolyl acetate.

During the rearrangement some of the acetylium ion was lost, but by addition of acetyl chloride during the transformation the yield of *p*-hydroxy-ketone was increased to a maximum of 87%.

Although the Fries rearrangement is a reaction of great experimental importance, its precise mechanism has not yet been satisfactorily elucidated. Von Auwers and Mauss [1] regard it as intramolecular; Skraup and Poller [2] claim that it is not a true rearrangement at all, but that the ester is first split into phenol and acyl chloride which then react by means of a normal Friedel–Crafts synthesis. Rosenmund and Schnurr,[3] however, consider that one mol. of ester reacts with a second, the acyl group in each case migrating to the other nucleus, thus yielding 2 mols. of hydroxy-ketone. More recently Baltzly, Ide, and Phillips [4] expressed the view that scission of the ester first takes place, with the formation of an acyl cation which then attacks the aromatic nucleus to yield the hydroxy-ketone.

In the present work the rearrangement of *o*-tolyl acetate was carried out in nitrobenzene solution, titanium tetrachloride being used as catalyst. Under these conditions the reaction took place homogeneously and this allowed its mechanism to be studied quantitatively.

EXPERIMENTAL

Materials.—The materials were purified by standard methods.

Rearrangement of o-*Tolyl Acetate.*—The apparatus consisted of a three-necked flask. To one neck a reflux condenser was attached, and to another a graduated tube fitted with a tap, for the titanic chloride. The centre neck was fitted with a mercury seal and glass stirrer, and agitation was continued throughout each experiment. The usual precautions were taken to exclude moisture; all-glass apparatus is advisable.

Nitrobenzene and *o*-tolyl acetate were introduced into the flask which was cooled in ice. The catalyst was then added gradually during 2 min. The reaction vessel was next placed in a thermostat, regulated to ±0·1°. At the end of the requisite time the vessel was immersed in ice for a few minutes, the contents were then decomposed with 4N-hydrochloric acid and transferred to a separating funnel, and the flask was washed out with a further quantity of dilute acid, the washings being added to the former liquid. The mixture in the funnel was shaken and gradually separated into two layers. The lower, nitrobenzene layer was removed and washed twice with dilute hydrochloric acid. Next the combined aqueous layers were

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[1] Von Auwers and Mauss, *Annalen*, 1928, **464**, 293.

[2] Skraup and Poller, *Ber.*, 1924, **57**, 2033.

[3] Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56.

[4] Baltzly, Ide, and Phillips, *J. Amer. Chem. Soc.*, 1955, **77**, 2522; cf. Hauser and Mann, *J. Org. Chem.*, 1952, **17**, 390.

shaken three times with ether, and the extract was added to the organic layer. This was shaken with 2N-sodium hydroxide until the alkaline extract had taken up all the 4- and 2-hydroxy-3-methylacetophenone, together with the *o*-cresol, leaving any unchanged ester in the nitrobenzene layer. Apart from a little resin and traces of other products, no other compounds were formed in the reaction. The alkaline extract was then filtered, if necessary, from any titanium hydroxide, and the filtrate distilled with steam to remove ether and nitrobenzene. The residual liquor from the distillation was made acid with concentrated hydrochloric acid and steam-distilled, 2-hydroxy-3-methylacetophenone and *o*-cresol being driven over. The residue from the steam-distillation, which contained the *p*-hydroxy-ketone, was filtered through glass wool while hot to remove the resin, and the latter was further extracted with small quantities of boiling water. The product separated from the filtrate, on cooling, as colourless prisms; these were washed with a little water and dried to constant weight; the m. p. was 104°.[5] The mother-liquid was then made up to a known volume, and to an acidified aliquot portion a slight excess of 2 : 4-dinitrophenylhydrazine (3 g. per 100 c.c. of concentrated sulphuric acid) was added. This precipitated the 2 : 4-*dinitrophenylhydrazone* of the *p*-hydroxy-ketone as red prisms, m. p. 276° (decomp.) (Found : N, 16·8. $C_{15}H_{14}O_5N_4$ requires N, 17·0%). Addition of the same reagent to the acidified steam-distillate precipitated the 2 : 4-dinitrophenylhydrazone of the *o*-hydroxy-ketone. After 6 hr. it was filtered off, washed with dilute hydrochloric acid, and dried. It consisted of red plates, m. p. 252°.[6] The filtrate was treated with excess of a solution of bromine in potassium bromide, and the precipitate of 4 : 6-dibromo-*o*-cresol (OH = 1) was filtered off after 1 hr., and dried.

The ether was removed by distillation from the nitrobenzene portion, which was then boiled under reflux for 2 hr. with a few c.c. of ethanol and 250 c.c. of 2N-sodium hydroxide. The nitrobenzene was distilled off in steam, and the residual liquor acidified with concentrated hydrochloric acid and again steam-distilled. The distillate contained *o*-cresol formed by the hydrolysis of the unchanged *o*-tolyl acetate. The cresol was estimated as described above.

The resinous product collected on the glass wool was extracted with acetone from which it was obtained by evaporation of the solvent (Found : *M*, cryoscopic in nitrobenzene and ebullioscopic in acetone : mean, *ca.* 300). It was soluble in sodium hydroxide solution.

Mixtures were made up containing known amounts of the reaction components in similar concentrations to those found in the actual rearrangement experiments. The results obtained on analysis were reproducible to ±2%, but were always lower, though never more than 4% lower, than the theoretical values. This is satisfactory in view of the difficulties involved in the analysis.

When solutions of titanic chloride in nitrobenzene were kept at 30° or more for a short time, a crust tended to be formed in the neck of the flask. In one such experiment where the titanium halide (0·1 mole) was dissolved in nitrobenzene (100 c.c.) this crust was forced into the liquid, *o*-tolyl acetate (0·1 mole) added, and the reaction allowed to proceed for 6 hr. at 30°. The yields of products formed by this method were very similar to those obtained by adding catalyst and ester simultaneously to the solvent.

Action of Heat on a Mixture of Titanium Tetrachloride and Acetyl Chloride.—Titanium tetrachloride (19·0 g., 0·1 mole) and acetyl chloride (7·85 g., 0·1 mole) were mixed at 0°. The yellow crystalline product was warmed slowly on the water-bath. The solid melted at about 20° and evolution of hydrogen chloride began at about 60°. The mixture first became red and liquid slowly began to distil over. A dark carbonaceous mass was formed in the flask. The bath was kept at the b. p. until no more liquid distilled; this consisted of acetyl chloride (3—4 g.).

In a similar experiment where the ingredients were dissolved in nitrobenzene (25 c.c.), the liquid became very dark and acetyl chloride (2 g.) was recovered by distillation. When titanic chloride (0·1 mole) and acetyl chloride (0·1 mole) in nitrobenzene (50 c.c.) were first heated at 50° for 7 hr. no acetyl chloride remained. Moreover, a number of rearrangements were carried out under different conditions, after which the resulting products were examined in order to ascertain if any acetyl chloride was present. In no case was its presence observed. Further, no acetyl chloride could be obtained by distillation from a nitrobenzene solution in which the titanic chloride-catalysed transformation of *o*-tolyl acetate had taken place.

Action of Titanium Tetrachloride on 4-*Hydroxy*-3-*methylacetophenone.*—Titanic chloride (0·1 mole) was added to the hydroxy-ketone (0·1 mole) in nitrobenzene (100 c.c.). After the

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[5] Cf. Klingel, *Ber.*, 1885, **18**, 2699.

[6] Cullinane, Lloyd, and Tudball, *J.*, 1954, 3894.

solution had been heated for (*a*) 3 hr., (*b*) 48 hr., and (*c*) 3 weeks, at 30°, 99% of the ketone was recovered in every case.

Effect of Addition of Acetyl Chloride in the Fries Rearrangement.—When acetyl chloride (0·025 mole) was added to *o*-tolyl acetate (0·1 mole), titanic chloride (0·2 mole), and nitrobenzene (100 c.c.), and the whole heated at 30° for 9 hr., the yields of 4-hydroxy-3-methylacetophenone and of *o*-cresol were 78% and 0% respectively. Without addition of the acyl chloride the yields were 75% and 15% respectively.

When the ester (0·1 mole), catalyst (0·2 mole), and nitrobenzene (150 c.c.) were kept at 30° for 19 hr., the yields of *p*-hydroxy-ketone and *o*-cresol were 78% and 13% respectively. When a similar mixture was kept at 30° for 14 hr., then acetyl chloride (0·15 mole) added, and the reaction mixture kept at 30° for a further 5 hr., the yields were 87% and 0% respectively. Similar results were obtained in another experiment, where the components were mixed in the exact amounts which had previously been found to be present after 14 hr. at 30°, acetyl chloride was added in an amount equivalent to the *o*-cresol present, and the reaction allowed to proceed for a further 5 hr.

Action of Titanium Tetrachloride on o-*Cresol and Acetyl Chloride.*—Titanium tetrachloride (0·1 mole) was added to a mixture of acetyl chloride (0·1 mole) and *o*-cresol (0·1 mole) in nitrobenzene (50 c.c.), and the reaction carried out at 30° under the same conditions as when the ester (0·1 mole) was the initial material. The yield of the *p*-hydroxy-ketone so obtained was slightly (7%) greater than in the corresponding reaction where the ester (0·1 mole) was used in place of acetyl chloride (0·1 mole) and *o*-cresol (0·1 mole) (see Fig. 6). The *o*-cresol and ester present at the end of the experiment were, however, unchanged in amount.

The following experiments were also carried out : (*a*) the catalyst (0·1 mole) was added at 0° to the cresol (0·1 mole) and the acyl chloride (0·1 mole) dissolved in nitrobenzene (100 c.c.), and the solution was kept at 30° for 6 hr.; (*b*) acetyl chloride (0·1 mole), titanic chloride (0·1 mole), and nitrobenzene (100 c.c.) were kept at 30° for 18 hr., whereupon *o*-cresol (0·1 mole) was added, and the whole kept at 30° for a further 6 hr.; (*c*) the reaction was carried out as in (*b*) except that the catalyst, acid chloride, and solvent were kept at 30° for 45 hr. before the *o*-cresol was added; (*d*) a similar reaction to (*b*) was carried out except that 4-hydroxy-3-methylacetophenone (1 g., 0·0067 mole) was added initially. The composition of the products resulting from these experiments was as follows :

o-Tolyl acetate	*o*-Cresol	4-Hydroxy-3-methylacetophenone
(*a*) 22·2%	16·0%	47·6%
(*b*) 24·2	30·8	36·5
(*c*) 16·2	45·5	28·0
(*d*) 17·3	40·3	20·0

Catalyst–Ester Ratio of 1·5 : 1.—The following results were obtained when the molar ratio of catalyst to ester was 1·5 : 1, the temperature being 30° and the volume of nitrobenzene 150 c.c.

Time (hr.)	*o*-Tolyl acetate	*o*-Cresol	4-Hydroxy-3-methylacetophenone	2-Hydroxy-3-methylacetophenone
4	15·4%	19·8%	54·8%	2·5%
9	4·4	15·4	68·5	2·9

DISCUSSION

Solutions containing Titanium Tetrachloride and o-*Tolyl Acetate in a Molar Ratio of* 1 : 1.—(i) *Reaction products.* The reaction between titanic chloride and *o*-tolyl acetate in nitrobenzene solution was studied at 20°, 30°, 40°, and 60°. The progress of the reaction at a given temperature was followed by experiments carried out for different times. In Figs. 1*a*, 1*b*, and 1*c*, the concentrations of the main constituents of the reaction mixture (expressed as mole % of initial ester) at 30° are plotted against time for a homogeneous solution obtained by dissolving *o*-tolyl acetate (0·1 mole) and titanium tetrachloride (0·1 mole) in nitrobenzene (50 c.c.). The results for 20°, 40°, and 60° fall into line (Figs. 3*a*, 3*b*, and 3*c*). In addition to these main constituents small quantities of 3-methyl-2-hydroxy-, -2-acetoxy-, and -4-acetoxy-acetophenone and a resinous material were formed. Moreover, since the points obtained on these curves are the results of individual experiments, the smoothness of the curves is very good evidence that minute traces of impurities, such as water or hydrogen chloride, have no effect on the course of the reaction.

(ii) o-*Tolyl acetate.* It is seen that the ester disappears smoothly. At the higher temperature the acetate reacts completely and the rate increases considerably with rise in temperature (Fig. 3*a*). At 20° and 30°, however, the acetate gradually disappears until there is 6—8% left after which, within the accuracy of our experiments, there is no further change with time.

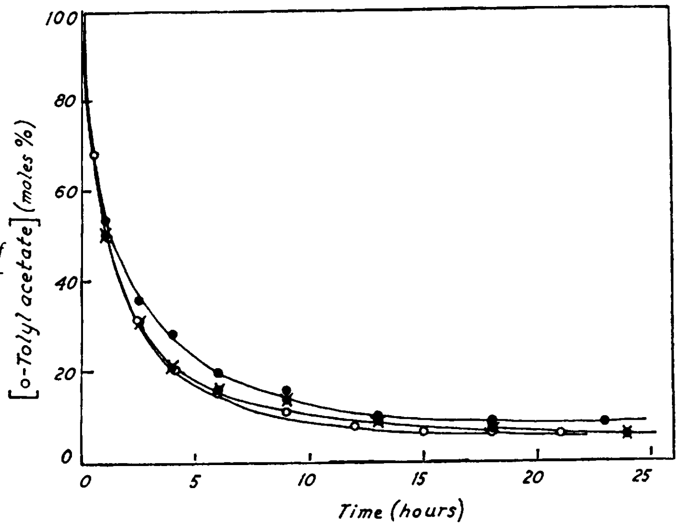


FIG. 1*a*. *Rate of disappearance of* o-*tolyl acetate at different concentrations* (*temp.* = 30°).

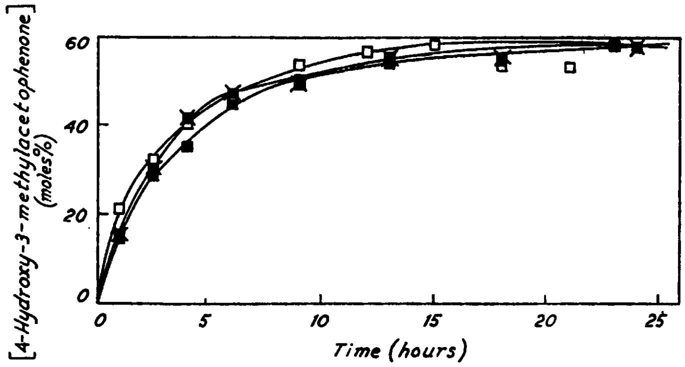


FIG. 1*b*. *Rate of formation of* 4-*hydroxy*-3-*methylacetophenone at different concentrations* (*temp.* = 30°).

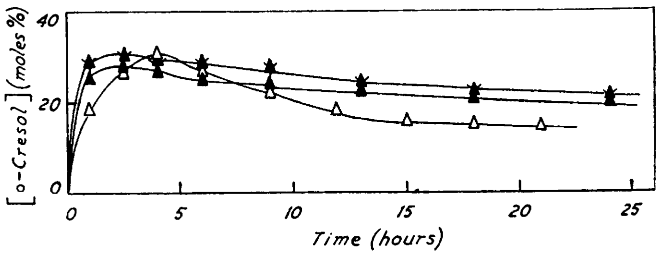


FIG. 1*c*. *Rate of formation of* o-*cresol at different concentrations* (*temp.* = 30°).

Initial materials : *o*-tolyl acetate (0·1 mole), titanium tetrachloride (0·1 mole). Nitrobenzene: Fig. 1*a*, ○ 50 c.c., ✱ 100 c.c., ● 150 c.c.; Fig. 1*b*, □ 50 c.c., ✱ 100 c.c., ■ 150 c.c.; Fig. 1*c*, △ 50 c.c., ✱ 100 c.c., ▲ 150 c.c.

The effect of a 3-fold change in the volume of nitrobenzene on the disappearance of *o*-tolyl acetate was examined at 30° and the results obtained are given in Fig. 1*a*. It is seen that the curves showing the disappearance of the ester are very similar at the three dilutions. Since the change in the concentrations of both ester and catalyst over this range is 3-fold, this behaviour can only mean that the catalyst combines with the tolyl acetate immediately on mixing, and that the disappearance of the latter is due to the first-order reaction of this ester-catalyst complex. [If the rate-determining step for the

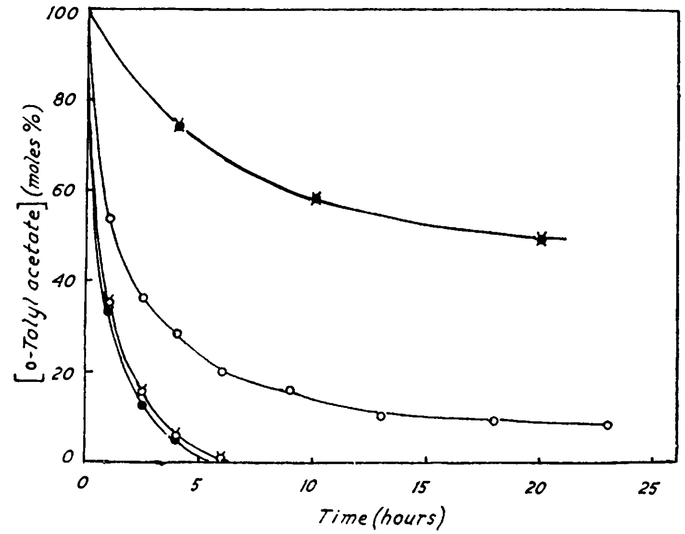


FIG. 2*a*. *Rate of disappearance of* o-*tolyl acetate for different ratios of catalyst to ester* (*temp.* = 30°).

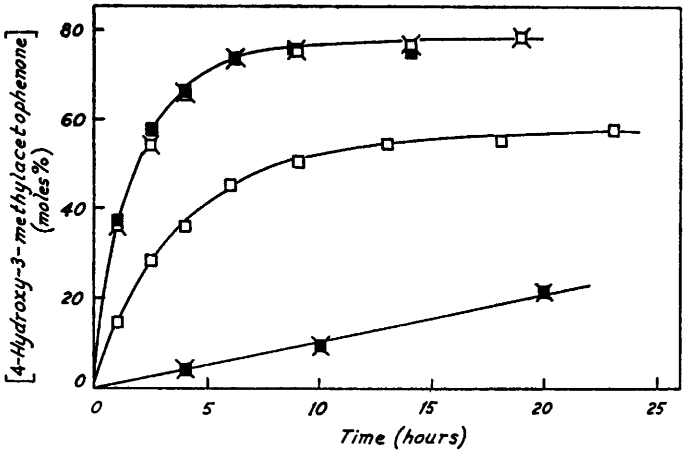


FIG. 2*b*. *Rate of formation of* 4-*hydroxy*-3-*methylacetophenone for different ratios of catalyst to ester* (*temp.* = 30°).

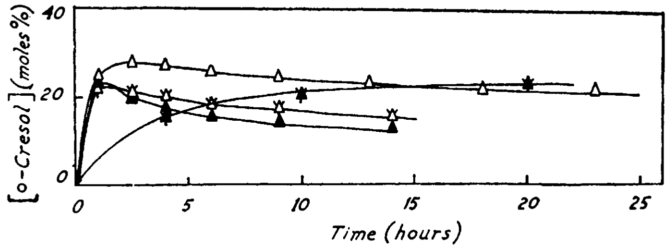


FIG. 2*c*. *Rate of formation of* o-*cresol for different ratios of catalyst to ester* (*temp.* = 30°).

Initial materials : *o*-tolyl acetate (0·1 mole), nitrobenzene (150 c.c.). Titanium tetrachloride: Fig. 2*a*, ✱ 0·05 mole, ○ 0·1 mole, ☆ 0·2 mole, ● 0·3 mole; Fig. 2*b*, ✱ 0·05 mole, ☐ 0·1 mole, ⌘ 0·2 mole, ■ 0·3 mole; Fig. 2*c*, ✱ 0·05 mole, △ 0·1 mole, ☆ 0·2 mole, ▲ 0·3 mole.

disappearance of ester were due to the second-order reaction between it and the titanic halide, or to a reaction between two molecules of ester–catalyst complex, this decrease in concentration would result in a 3-fold decrease in the initial slope of the reaction curve

(Fig. 1*a*) whereas it is seen that this decrease in concentration does not affect the shape of the reaction curve, within experimental error.] The same result was obtained at 40° for a 2-fold change in the concentration of acetate and titanic chloride.

(iii) o-*Cresol.* The shape of the *o*-cresol curve (Fig. 1*c*) shows that the cresol is produced

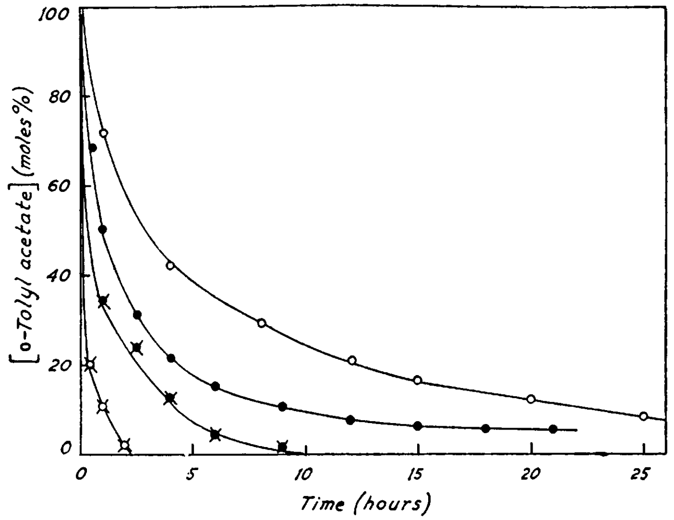


FIG. 3*a*. *Rate of disappearance of* o-*tolyl acetate at different temperatures.*

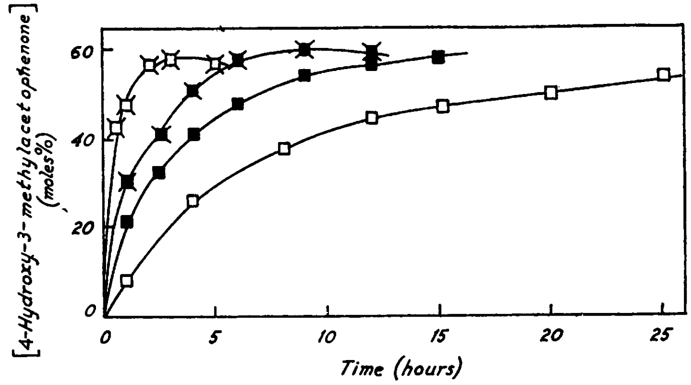


FIG. 3*b*. *Rate of formation of* 4-*hydroxy*-3-*methylacetophenone at different temperatures.*

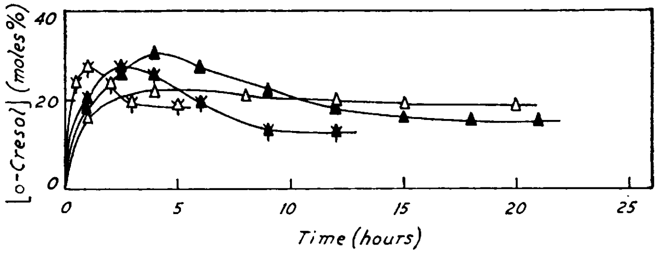


FIG. 3*c*. *Rate of formation of* o-*cresol at different temperatures.*

Initial materials: *o*-tolyl acetate (0·1 mole), titanium tetrachloride (0·1 mole), nitrobenzene (50 c.c.). Fig. 3*a*, ○ 20°, ● 30°, ✱ 40°, ⌧ 60°; Fig. 3*b*, □ 20°, ■ 30°, ▣ 40°, ⌧ 60°; Fig. 3*c*, △ 20°, ▲ 30°, ✱ 40°, ☆ 60°.

directly from the tolyl acetate, since the slope of the curve is finite at zero time. Further, since this curve has a maximum, the cresol undergoes reaction into another compound (there is evidence that this is the *p*-hydroxy-ketone) which causes its concentration to fall again. The shape of this curve is typical for such consecutive reactions. This behaviour was observed at all the temperatures studied (Fig. 3*c*).

(iv) 4-*Hydroxy*-3-*methylacetophenone.* This ketone is produced at a finite rate at zero time (Fig. 1*b*). This establishes that it results directly from the tolyl acetate–titanium tetrachloride complex (which is formed immediately at zero time) by an *intramolecular* change. If the whole of the ketone were produced from the *o*-cresol by an *intermolecular* reaction the slope of its concentration curve would be zero at zero time, since at that time the concentration of cresol is zero. This behaviour is found at all the temperatures studied (Fig. 3*b*).

(v) *Conversion of* o-*cresol into* 4-*hydroxy*-3-*methylacetophenone.* The fall in the *o*-cresol concentration after it had reached its maximum value (Fig. 1*c*) shows that it is subsequently converted into another compound. This product is presumably the *p*-hydroxy-ketone, since in some cases we find that the concentration of the latter continues to increase after the tolyl acetate has completely disappeared but in the region where the cresol curve is still decreasing (Figs. 2*a*, 2*b*, and 2*c*).

Variation in Titanium Tetrachloride–o-*Tolyl Acetate Ratio.*—Experiments were carried out for titanic chloride–*o*-tolyl acetate molar ratios of 0·5, 1, 2, and 3 at 30° and the results are shown in Figs. 2*a*, 2*b*, and 2*c*. From these the following points can be made. (*a*) An increase in the catalyst–ester ratio increases the rate of reaction and also the amount of *p*-hydroxy-ketone formed in the reaction as far as a catalyst–ester ratio of 2, after which further increase in the ratio has no effect on the rate of reaction or on the yields of products, since the curves obtained for the ratios of 2 and 3 are almost identical. (*b*) As the catalyst–ester ratio increases, the rate of disappearance of *o*-tolyl acetate also increases until for ratios of 2 or more all the original ester undergoes rapid conversion into reaction products (Fig. 2*a*). (*c*) The fact that once the catalyst–ester ratio of maximum effect, *i.e.*, 2, is reached, the rate of disappearance of ester is almost unchanged for a further increase in catalyst–ester ratio, again shows that this disappearance is not due to a bimolecular reaction between catalyst and ester, for, if such were the case, the change in ratio from 2 to 3 would markedly increase the rate of disappearance of the starting material. It shows, on the other hand, that the catalyst combines immediately with the ester and that it is the rate of decomposition of this complex which is measured.

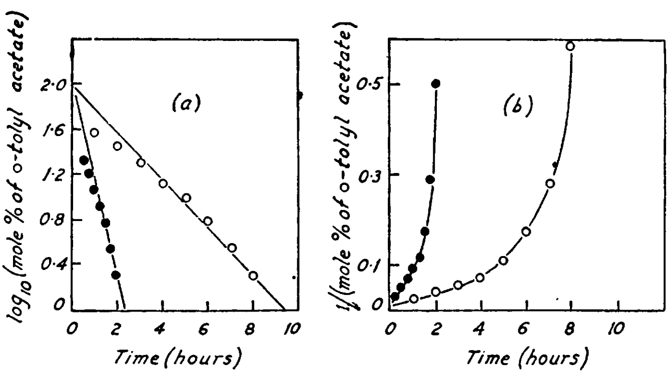


FIG. 4. *Order plots for disappearance of* o-*tolyl acetate;* (*a*) *first order;* (*b*) *second order.*
○ 40°, ● 60°.

With a catalyst–ester molar ratio of 1·5 the yields of *p*-hydroxy-ketone were intermediate between those obtained when the ratios were 1 and 2.

Effect of Temperature.—The results of the experiments carried out at 20°, 30°, 40°, and 60° for a catalyst–ester ratio of 1 are shown in Figs. 3*a*, 3*b*, and 3*c*. It is seen that as the temperature rises there is a marked increase in the reaction rate. For this catalyst–ester ratio of unity, the ester disappears completely at 40° and 60°. The curves for this disappearance have been analysed by plotting the first-order relationship $\log_{10}$ (mole % of ester) against time, and in Fig. 4*a* the plots obtained at 40° and 60°, at which temperatures the ester reacts to completion, are shown. These curves show deviations from straight-line plots, but it is found that for the catalyst–ester ratios of 2 : 1 and 3 : 1, these plots approximate much more closely to straight lines. In Fig. 4*b*, we give the second-order plots of 1/(mole % of ester) against time for comparison with the first-order plots in Fig. 4*a*.

These second-order plots are very markedly curved, and this affords additional evidence to that given in an earlier section, that the disappearance of the ester is of first order. The first-order constants *k* (sec.$^{-1}$) have been obtained from the slopes of the first-order plots. In Fig. 5, $\log_{10}k$ is plotted against $1/T$, and the slope of this line gives an activation energy for the disappearance of *o*-tolyl acetate of 14·3 kcal. per mole. An alternative determination of the activation energy has been made with values of *k* calculated by the method of initial slopes (see Fig. 5), and the activation energy so obtained is 15·2 kcal. per mole. The mean of these two values for the activation energy of the disappearance of ester is 14·8 ± 0·5 kcal. per mole. In view of the complexity of this reaction, these methods of determining *k* are somewhat approximate. The best values will be those obtained from the initial slopes.

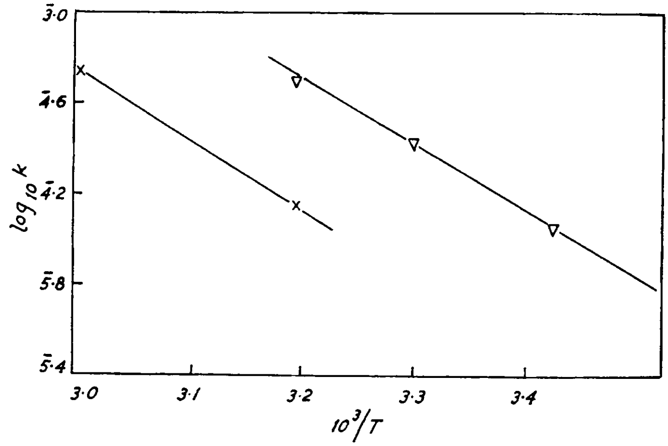


FIG. 5. *Dependence of k on temperature.*

k obtained from first-order plots (×), and initial slopes (▽).

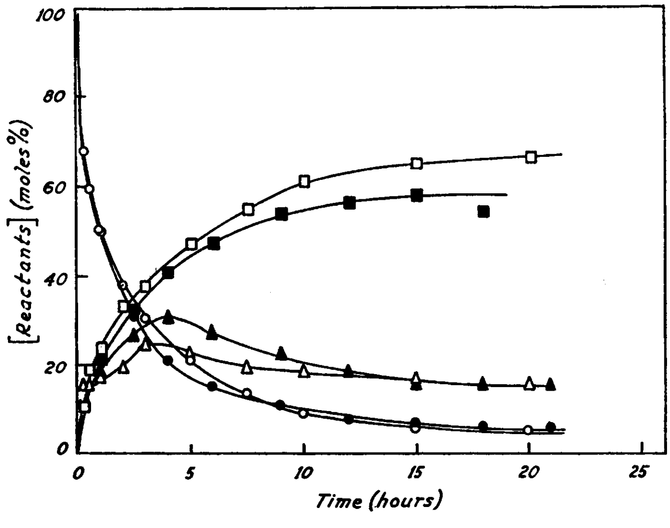


FIG. 6. *Reaction between* o-*creso and acetyl chloride in presence of titanium tetrachloride* (*temp.* = 30°).

Initial materials: (*a*) *o*-cresol (0·1 mole), acetyl chloride (0·1 mole), titanium tetrachloride (0·1 mole), nitrobenzene (50 c.c.); ○ *o*-tolyl acetate, △ *o*-cresol, □ 4-hydroxy-3-methylacetophenone; (*b*) *o*-tolyl acetate (0·1 mole), nitrobenzene (50 c.c.); ● *o*-tolyl acetate, ▲ *o*-cresol, ■ 4-hydroxy-3-methylacetophenone.

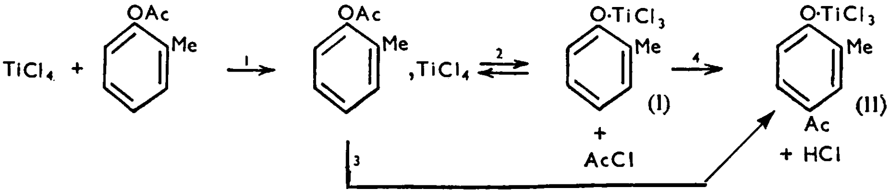
Action of Titanium Tetrachloride on 4-Hydroxy-3-methylacetophenone.—Experiments described above show conclusively that no reaction takes place between the catalyst and the hydroxy-ketone to form ester or cresol.

Action of Titanium Tetrachloride on o-*Cresol and Acetyl Chloride.*—The reaction at 30° between a 1 : 1 : 1 molar mixture of *o*-cresol, titanic chloride, and acetyl chloride, described above, is similar to the corresponding reaction between *o*-tolyl acetate and the titanic halide (Fig. 6). At the earliest possible time of analysis the system behaves much as if the initial material were the ester. The close similarity of the two reactions shows that hydrogen chloride has no effect on the reaction since, at the time represented by the first points on the curve, an amount of hydrogen chloride has been formed equal to 70 mole % of the initial cresol.

Although *o*-cresol is seen to be converted into the hydroxy-ketone during the reaction and, as shown above, the latter is not converted into *o*-cresol under the conditions of the reaction, nevertheless we find that about 15—20% of the cresol does not react. This suggests that the acetylium ion disappears during the course of the reaction and that at the end none is left. That such is the case has been demonstrated, for attempts to recover it by distillation from a mixture of titanic chloride and acetyl chloride in nitrobenzene show that very little or none of the acetyl chloride can be recovered from such mixtures. This result is not unexpected, for it is known [7] that acetyl chloride reacts in the presence of aluminium chloride to form condensation compounds in some of which the aluminium is present in combination.

Further experiments described above on the effect of added acetyl chloride show clearly that: (*a*) under conditions where it is certain that the acyl chloride is present no *o*-cresol is left at the end of the rearrangement; (*b*) mixtures of acetyl chloride and titanium tetrachloride react to a smaller extent with *o*-cresol the longer they are allowed to stand before the cresol is added; (*c*) the disappearance of acyl chloride is accelerated by the presence of the *p*-hydroxy-ketone, owing to its reaction with this compound.

Mechanism of the Reaction.—Any mechanism suggested to explain these results must take account of the following facts. (*a*) The titanic chloride combines instantaneously with the *o*-tolyl acetate, and it is the subsequent first-order reaction of this complex that is measured. (*b*) The *o*-cresol is formed directly from the *o*-tolyl acetate. (*c*) The 4-hydroxy-3-methylacetophenone is formed directly from the *o*-tolyl acetate. (*d*) The *o*-cresol undergoes further reaction, presumably to the 4-hydroxy-3-methylacetophenone. (*e*) The reaction rate increases with increase in the catalyst–ester ratio up to a value of 2, after which increase in the ratio has scarcely any effect. These results may be interpreted as in the annexed scheme.



Reaction (1) as shown is irreversible. Complexes of this type with Friedel–Crafts catalysts are known; *e.g.*, titanic chloride forms a 1 : 1 addition compound with phenyl acetate.[8] Reaction (2) involves the scission of a carbon–oxygen bond by means of the titanic chloride. Compounds of type (I) are known to be readily prepared from phenol and titanium tetrachloride; *e.g.*, phenoxytitanium trichloride, $C_6H_5{\cdot}O{\cdot}TiCl_3$, was obtained in this way by Luchiinski and Altmann.[9] This reaction is shown as reversible because of our results on *o*-cresol, acetyl chloride, and titanium tetrachloride systems. It is at first sight surprising that, for a 1 : 1 : 1 molar mixture of *o*-cresol, titanic chloride, and acetyl chloride, the *o*-cresol should fall rapidly to about 17% and subsequently rise to a maximum of about 25% (see Fig. 6). This subsequent rise of 8% we attribute to the continuous disappearance of acetyl chloride during the reaction. We have given evidence above for this disappearance in explaining the fact that *o*-cresol remains at the end of our experiments in spite of the irreversibility of the hydroxy-ketone formation. Reaction (3) is required by the observed fact that the hydroxy-ketone is formed at a finite rate at the start of the experiment by the first-order disappearance of the ester, and this observation

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[7] Combes, *Compt. rend.*, 1886, **103**, 814; *Ann. Chim.* (*France*), 1887, **12**, 204; Gustavson, *J. prakt. Chem.*, 1888, **37**, 109; Wedekind, *Annalen*, 1902, **232**, 246.

[8] Cullinane and Lewis, unpublished work.

[9] Luchiinski and Altmann, *Z. anorg. Chem.*, 1935, **225**, 321.

establishes that the migration of the acetyl group from the phenolic oxygen to the *para*-carbon atom can occur by an *intramolecular* process. This is further supported by the fact that for a 1 : 1 catalyst–ester ratio, a three-fold change in the volume of solvent has very little effect on the initial slope of the curves in Fig. 1*b*. Reaction (4) is required to account for the conversion by an intermolecular process of the *o*-cresol or its derivative (I) into the hydroxy-ketone or its derivative (II), which would be hydrolysed subsequently to the hydroxy-ketone itself.

The striking result that a maximum effect is observed for a catalyst–ester ratio of 2 suggests that a more reactive 2 : 1 catalyst–ester complex may be formed in the presence of excess of catalyst by attachment of catalyst at each of the two oxygen atoms of the ester. Further, the products of reactions (2) and (3) can take up a catalyst molecule in addition to that shown in the above scheme, owing, in the case of reaction (3), to the fact that the hydroxy-ketone has two possible points of attachment for catalyst, and in the case of reaction (2) to the fact that the acetyl chloride produced will form a complex with a mol. of catalyst to form $CH_3{\cdot}CO^+\ TiCl_5^-$. It has been found that such a 1 : 1 complex can be readily prepared from acetyl chloride and the titanic halide.[10]

Our results also show that in order to obtain the maximum yield of hydroxy-ketone sufficient catalyst and acyl chloride must be present.

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[10] Cullinane, Chard, and Leyshon, *J.*, 1952, 4106.