417. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part IV. Preliminary Kinetic Data on the Acylation of Aromatic Compounds by Pivaloyl Chloride.*

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The acylation of aromatic compounds by tertiary acid halides in presence of aluminium chloride as a catalyst is simultaneous with alkylation, and no simple order for the rate of the reaction between pivaloyl chloride and anisole has been found. Analysis of the kinetic values is the more difficult because of complex formation between aluminium chloride and the ketonic product which causes loss of catalytic efficiency, this affecting differently the rates of alkylation and acylation. There is reason for believing that, when the concentration of the catalyst drops below 0·025 g.-mol./l., the rate of acylation is negligibly small, so that only alkylation occurs after this point. Under the conditions used, graphic representation of the results indicates that only alkylation occurs when toluene is substituted for anisole. The times measured for 10% and 25% change under identical conditions using benzene, toluene, and anisole, respectively, as the aromatic components are greatest for anisole, and it can therefore be tentatively assumed that the rate-determining step for the above reactions is that of complex formation between the catalyst and acid halide.

A KINETIC study of the simultaneous alkylation and acylation of aromatic compounds, such as very often occur when *tertiary* acids and their derivatives are used, presents particular difficulties because the concentration of the catalyst, which remains approximately constant for alkylation, is effectively reduced when a ketone is produced owing to the formation of a stable complex with the product. The added difficulty that the velocity constant for alkylation is proportional to the square of the concentration of the catalyst necessitates accurate determination of all the products formed during the reaction. In his papers on the acylation of benzene with benzoyl halides, Olivier (for references see preceding paper) showed that in an *excess* of hydrocarbon a first-order reaction occurred, the rate of which was independent of the initial concentration of the acid halide but not of that of the catalyst. Owing to the formation of a complex with the ketone, referred to above, only one molecule of the acid chloride was transformed by the aluminium chloride, this being true when a limited quantity of benzene in carbon disulphide solution was used. In the latter case, the rate was proportional to the concentrations of both the acid halide (or the acid halide–catalyst complex) and the hydrocarbon, *i.e.*, a second-order constant was obtained, and there was some evidence that a constant proportional to the square of that of the benzene fitted the data. With regard to the aluminium chloride or bromide, Olivier found that the first-order velocity constant was multiplied by 1·3 when the initial catalyst concentration was doubled.

It has not yet been found possible to carry out complete kinetic analyses and indeed at present we do not require them. The results so far obtained have, however, made it possible to make certain tentative deductions. Before considering the actual determinations reference should be made to the influence, on alkylation, of formation of the complex between the catalyst and ketone because it could not be assumed *a priori* that this would be associated with loss of catalytic efficiency as in the case of acylation (Part III, preceding paper; Olivier, *loc. cit.*). Inspection of the kinetic results might well be considered to indicate the contrary. A qualitative test has been performed by adding an excess of pivaloyl chloride to a solution of methoxyphenyl *tert.*-butyl ketone in benzene containing about two-thirds of a mole of aluminium chloride per mole of ketone. There was no visible reaction until the concentration of aluminium chloride was raised to that of the ketone. It was therefore concluded that uncombined aluminium chloride is essential for alkylation, as for acylation.

The relevance of the foregoing is seen in the curves obtained when pivaloyl chloride is condensed with anisole, the proportions of the reactants being shown in Table I.

In each case there was an initial rapid reaction, followed by a slow one, which appeared as a straight-line relation between the logarithm of the acid chloride concentration and the time, the slope being nearly identical for the three experiments. The general appearance of the curves is similar to those described in Part III, but the steep curved portions are much longer in the present instances. If from the qualitative experiment outlined earlier in the paper it is assumed that no reaction would take place if *all* the catalyst had been used in forming the ketone–catalyst complex, it would seem reasonable to suppose that acylation ceases when the aluminium chloride has reached a certain minimum figure, in this case approximately 0·025 g.-mol./l. Experiment " B " was repeated at the boiling point (in order to ensure complete reaction) using identical concentrations. The yield of ketone actually isolated was 20% (based on the acid chloride), corresponding to nearly 62% of the original aluminium chloride.

TABLE I.

Friedel–Crafts condensation of pivaloyl chloride with anisole.

Experiment:	" B."	" C."	" D."
Initial $[AlCl_3]$ (g.-mol./l.)	0·063	0·063	0·064
$[CMe_3{\cdot}COCl]$ (g.-mol./l.)	0·314	0·315	0·063
[Anisole] (g.-mol./l.)	solvent	0·315	0·063
Reaction medium	anisole	CS_2	CS_2
$10^2 \times k_1^{20}$ *	0·046	0·042	0·051
Final $[AlCl_3]$ † (calc.) (g.-mol./l.)	0·025	0·022	0·027

* Calculated from the straight (middle) portion of the curve. (The curves flatten out slightly towards the end of the reaction.)

† Calculated from : $k_1 = 0{\cdot}43 \times [AlCl_3]^2 + 0{\cdot}0002$.

It may be observed that only when anisole was the solvent did the gram-molecular quantity of acid chloride converted, into what was presumably a mixture of hydrocarbon and ketone, exceed that of the aluminium chloride. Anisole is a medium in which both reactions may be expected to be accelerated and, though with the increase of the rate of ketone formation the amount of hydrocarbon would decrease owing to its dependence on the square of the concentration of the catalyst, nevertheless it is possible that, initially, relatively large amounts may be formed.

Ketone formation can thus be recognised by the type of curve obtained when the logarithm of the concentration of the acid chloride is plotted against time; a straight line would indicate its absence. It was mentioned in Part II (this vol., p. 1950) that very little ketone (less than 7%) was produced when 0·1 mol. of aluminium chloride was used with toluene; reduction of the catalyst concentration to 0·063 g.-mol./l. should lower that of the ketone to negligibly small proportions. This was reflected in the results obtained for toluene, which afforded a figure for $10^2 \times k_1^{20}$ (0·153) practically identical with that for benzene (0·151) measured under the same conditions.

In conclusion, we found that the overall rates for the various reactions, judged by the rate of disappearance of the acid chloride, are not very different from one another when the initial concentrations of the various components of the reactions are identical. This is shown in Table II.

TABLE II.

Time for 10% and 25% change in carbon disulphide solution.

$[AlCl_3] = 0{\cdot}063$ g.-mol./l.; [Aromatic compound] $= [CMe_3{\cdot}COCl] = 0{\cdot}314$ g.-mol./l.

Aromatic compound :	Benzene.	Toluene.	Anisole.
Time for 10% change (mins.)	50	43	98
Time for 25% change (mins.)	200	200	530

These figures appear to indicate that the rate-determining stage for the reaction may be the formation of the first complex (Part III) but the complexity of the kinetics of the two competitive reactions makes it preferable to treat such a deduction with reserve.

EXPERIMENTAL.

Qualitative Experiments.—Reaction between pivaloyl chloride and benzene in the presence of methoxyphenyl tert.*-butyl ketone.* Pivaloyl chloride (10 g., 0·079 mols.) in benzene (10 c.c.) was added to a stirred mixture of aluminium chloride (6 g., 0·045 mol.), methoxyphenyl *tert.*-butyl ketone (11·7 g., 0·061 mol.), and benzene (80 c.c.). There was no visible reaction at room temperature, and no gases were evolved even after several hours. When the mixture was heated to the b. p. there appeared to be an exceedingly slow reaction, the volume of the gases being hardly more than that required by the expansion of the air within the reaction vessel. The mixture was now cooled to room temperature, and a further quantity (3 g.) of aluminium chloride added such that there was now a very slight excess (0·006 mol.) compared with the ketone. The mixed gases (hydrogen chloride and carbon monoxide) were now liberated at *ca.* 100 c.c. per hour. A further addition of the catalyst (3 g.) immediately accelerated the reaction, and within a minute the whole of the carbon monoxide was eliminated, the total volume of gases collected being >2 l.

Reaction between pivaloyl chloride and anisole in the presence of low concentrations of aluminium chloride (cf. *determination* C). The acid chloride (3·4 g.), anisole (3 g.), aluminium chloride (0·8 g.), nitrobenzene (8 c.c.), and carbon disulphide (75 c.c.) were heated to the b. p., and the carbon monoxide collected for identification, but no attempt was made to measure its volume. Approx. 1·1 g. (20%) of *p*-methoxyphenyl *tert.*-butyl ketone, b. p. 160°/18 mm., was isolated and identified by its semicarbazone, m. p. 150—151° (Part II).

Kinetic Determinations.—The method used was that described in Part III. The aluminium chloride (initial concentration, 0·063 g.-mol./l., in every case except the last) was dissolved in nitrobenzene (20 ml.) before addition to the reaction mixture.

Experiment " A." Initial concns.: toluene, 0·314 g.-mol./l.; pivaloyl chloride, 0·314 g.-mol./l. Solvent : carbon disulphide.

Time (min).	NaOH (ml.).	$CMe_3{\cdot}COCl$ (g.).	$CMe_3{\cdot}COCl$ (g.-mol./l.).	Log_{10} [$CMe_3{\cdot}COCl$].
0	29·5	0·373	0·308	$\bar{1}$·489
43	27·1	0·343	0·286	$\bar{1}$·456
201	22·0	0·279	0·232	$\bar{1}$·366
290	18·5	0·236	0·195	$\bar{1}$·291
511	13·6	0·171	0·141	$\bar{1}$·150
675	10·8	0·136	0·113	1·052

$$10^2 \times k_1^{20} = 0{\cdot}153.$$

The following table describes three condensations with anisole, the first with the anisole as solvent, the other two in carbon disulphide.

Experiment " B." Initial concns. : anisole, solvent; pivaloyl chloride, 0·314 g.-mol./l.

Time (min.).	NaOH (ml.).	$CMe_3{\cdot}COCl$ (g.).	$CMe_3{\cdot}COCl$ (g.-mol./l.).	Log_{10} [$CMe_3{\cdot}COCl$].
0	22·9	0·290	0·240	$\bar{1}$·380
72	20·4	0·257	0·213	$\bar{1}$·329
183	18·2	0·230	0·192	$\bar{1}$·283
304	17·2	0·221	0·183	$\bar{1}$·263
416	16·6	0·209	0·173	$\bar{1}$·238
452	16·2	0·204	0·170	$\bar{1}$·230

Experiment " C." Initial concns. : anisole, 0·315 g.-mol./l.; pivaloyl chloride, 0·315 g.-mol./l. Solvent : carbon disulphide.

0	30·0	0·380	0·315	$\bar{1}$·498
98	27·3	0·346	0·287	$\bar{1}$·458
199	26·9	0·341	0·283	$\bar{1}$·452
319	26·6	0·337	0·280	$\bar{1}$·447
530	26·2	0·333	0·276	$\bar{1}$·440

Experiment " D." Initial concns. : anisole, 0·063 g.-mol./l.; pivaloyl chloride, 0·063 g.-mol./l.; $AlCl_3$, 0·064 g.-mol./l. Solvent : carbon disulphide.

0	15·3	0·195	0·064	$\bar{2}$·806
91	12·4	0·157	0·052	$\bar{2}$·719
247	10·4	0·133	0·044	$\bar{2}$·647
358	9·5	0·121	0·040	$\bar{2}$·606
551	9·0	0·115	0·038	$\bar{2}$·580

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