876. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part IX.* Concentration and Environmental Factors influencing the Elimination of Carbon Monoxide from Pivaloyl Chloride.*

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The rate of elimination of carbon monoxide from pivaloyl chloride, catalysed by aluminium chloride is of the first order with respect to the concentration of the acid chloride and of the second in the concentration of catalyst. Unlike in ketone synthesis, the rate constant is unaffected by the ratio of aluminium chloride to acid chloride. Preliminary experiments show a 60—100% increase in the rate of reaction for a temperature rise of 2°, and an increase in the dielectric constant of the solvent also accelerates reaction. Although the rate of elimination of carbon monoxide is independent of the aromatic component, experiments in toluene demonstrate that this is not the case for ketone formation. It appears, from the examination of the two reactions in competition, that the probable rate-determining stage for elimination of carbon monoxide is the formation of the reactive complex from aluminium chloride and the acid derivative. Substitution of pivalic anhydride for pivaloyl chloride affords substantially unchanged reaction rates but some deactivation is apparent.

The kinetic results are discussed in relation to those obtained for Friedel–Crafts alkylations and acetylations by previous investigators. It is shown that the postulate of a preliminary equilibrium involving the catalyst, similar to that proposed by N. N. Lebedev, is justified, but structures for the catalyst and the catalyst–halide complex put forward by this author are rejected. In particular, deactivation, not activation, results from co-ordination of aluminium chloride by the oxygen atom of the acid halide.

DECOMPOSITION of pivaloyl chloride by aluminium chloride appears to be a first-order reaction with respect to the acid chloride although side-reactions lead to small variations in the value of the first-order constant.[1] Ketonic products which reduce the activity of the catalyst can in some cases be isolated.[2] Their formation depends on the composition of the solvent, the concentration of the acid chloride, and on the conditions.[3] Even in optimum conditions the *tert.*-butylbenzene obtained by the condensation of pivaloyl chloride and benzene exhibits a strong carbonyl absorption peak in the infrared spectrum. Though the presence of the ketone could not be detected by ordinary analytical methods, the possibility of its formation was inferred because the yields of carbon monoxide actually isolated were never greater than 80—90%.

Rothstein and Saville found [1] that for a particular concentration of catalyst the first-order constant was independent of the ratio of pivaloyl chloride to aluminium chloride

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* Part VIII, preceding paper.

[1] Rothstein and Saville, *J.*, 1949, 1954.

[2] Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 4169.

[3] Grundy, Hsü, and Rothstein, *J.*, 1952, 4136.

concentrations over the range 5—10 : 1. Except for very high ratios (Table 1, expts. 1, 2, 3, 4, and 88), the carbon monoxide method also shows that the rate constant is independent of both the initial concentration of the pivaloyl chloride and its concentration relative to that of the aluminium chloride.

It had been noted by Rothstein and Saville [1] that aluminium chloride entered the rate equation approximately as the square of its concentration. This was correspondingly the case for the elimination of carbon monoxide. The rate constants for a number of different concentrations of aluminium chloride (see Table 2) satisfy the equation (calculation 1), $k_1^{20\cdot36} = 0\cdot5879[\mathrm{AlCl_3}]^2 + 0\cdot000847$, but a much more accurate expression, particularly for smaller concentrations of catalyst (calculation 2) is: $k_1^{20\cdot36} = 0\cdot4928[\mathrm{AlCl_3}]^2 + 0\cdot025[\mathrm{AlCl_3}] - 0\cdot00037$. The justification for including a term involving the first power of catalyst concentration is discussed later. The reaction orders calculated from $n = (\log k - \log k')/(\log [\mathrm{AlCl_3}] - \log [\mathrm{AlCl_3}]')$ vary slightly from 1·80 for the lowest to 1·90 for most experiments.

TABLE 1. *Effect of variation in acid chloride concentration.*

Temp. for " A " = 20·36°; for " B " > 20·36°. " Carbon monoxide " method.

	" A "			" B "			
Expt. no.	(1, 2, 3, 4)	(8, 9)	11	88	87	86	85
[$\mathrm{CMe_3{\cdot}COCl}$] (mole/l.)	0·326	0·163	0·082	0·100	0·075	0·050	0·025
[$\mathrm{AlCl_3}$] (mole/l.)	0·063	0·063	0·063	0·050	0·050	0·050	0·050
10^2k_1 (min.$^{-1}$)	0·298	0·301	0·305	0·223	0·261	0·257	0·261

TABLE 2. *Effect of variation in catalyst concentration.*

Temp., 20·36°. " Carbon monoxide " method.

	[$\mathrm{AlCl_3}$]	10^2k_1 (min.$^{-1}$)				[$\mathrm{AlCl_3}$]	10^2k_1 (min.$^{-1}$)		
Expt. no.	(mole/l.)	Found	Calc. (1)	Calc. (2)	Expt. no.	(mole/l.)	Found	Calc. (1)	Calc. (2)
10	0·01575	0·029	0·099	0·011	24, 25, 26, 27	0·100	0·698	0·673	0·706
5, 6	0·0315	0·106	0·143	0·091	37	0·125	0·923	1·000	1·049
20, 21, 22	0·050	0·223	0·232	0·211	29, 30, 31	0·150	1·468	1·408	1·447
1, 2, 3, 4	0·063	0·298	0·318	0·317	32, 33	0·200	2·434	2·437	2·434
38	0·833	0·515	0·493	0·513	34, 35, 36	0·250	3·668	3·760	3·651

The existence of a rather steep temperature gradient for the reaction was confirmed by repeating some of the determinations at the standard temperature (20·36°) ± 2° (see Table 3). The higher temperatures were, in each case, associated with decreased side-reactions.

TABLE 3. *Effect of temperature on elimination of carbon monoxide.*

[$\mathrm{CMe_3{\cdot}COCl}$] (mole/l.)	0·326			0·326		0·025	
[$\mathrm{AlCl_3}$] (mole/l.)	0·0315			0·063		0·125	
Expt. no.	12	5	13, 16, 17	1—4	14, 15	37	18, 19
Temp.	19·36°	20·36°	22·36°	20·36°	22·36°	20·36°	22·36°
10^2k_1 (min.$^{-1}$)	0·095	0·110	0·179	0·298	0·507	0·923	2·01

TABLE 4. *Reaction constants in benzene and carbon tetrachloride.*

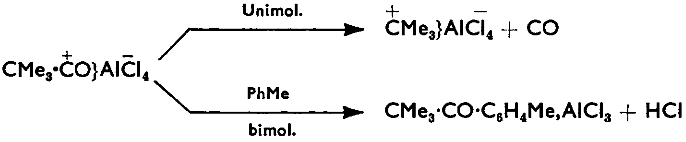
[$\mathrm{CMe_3{\cdot}COCl}$] = 0·326 mole/l. [$\mathrm{AlCl_3}$] = 0·063 mole/l.

			Time (min.)							Reaction
Expt. no.	Solvent		30	60	90	120	150	180	210	(%)
1	$\mathrm{C_6H_6}$–$\mathrm{Ph{\cdot}NO_2}$	10^2k_1 =	—	0·27	—	0·25	0·23	0·23	—	39
46	$\mathrm{CCl_4}$	10^2k_1 =	0·16	0·16	0·16	0·16	0·16	0·16	0·155	25
47	,,	10^2k_1 =	0·17	0·17	0·17	0·17	0·16	0·16	0·16	28

The possibility was next explored of using solvents other than the benzene–nitrobenzene mixture which had been employed hitherto, but it was found that the reactions in nitromethane or in *s*.-tetrachloroethane were slow and unreliable. Carbon tetrachloride afforded consistent results, and the curve obtained showed a complete absence of side-reactions (Table 4). The limited solubility of aluminium chloride, however, prevented a more extensive use of this solvent. The slow reaction rate is typical of that commonly noticed when non-polar solvents are used and will be referred to below.

The contrary was true of reactions in nitrobenzene. The initial vigorous evolution of gas was too great to be measured and ceased after a few minutes. The titration method showed that over 50% of the acid chloride had disappeared in the first few minutes and about 70% (0·22 mol.) in a little more than an hour. Cessation of the reaction resulted from the deactivation of the catalyst, and addition of a further quantity of a nitrobenzene solution of aluminium chloride restarted the decomposition. It is clear that the complex said to be formed from the catalyst and nitrobenzene can still accelerate the reaction. There was no accelerating effect when more of the acid chloride was added.

The next experiments were designed to compare the decomposition with ketone formation. Rothstein and Saville [4, 5] observed that pivaloyl chloride and toluene afford a mixture of *tert.*-butyl *p*-tolyl ketone and *p*-*tert.*-butyltoluene and it was postulated that whereas the first of these results from a first-order reaction with regard to toluene, the second arises from a reaction which is of zero order in this respect :



Thus by performing the reaction in carbon disulphide, with increasing concentrations of toluene, the ratio hydrocarbon : ketone should diminish, as is the case (Table 5).

TABLE 5. *Reaction between pivaloyl chloride and toluene, with various concentrations of toluene in carbon disulphide.*

Acid titration method. [CMe$_3$·COCl] = 0·50 mole/l. [AlCl$_3$] = 1·5 mole/l.

[PhMe] (mole l.)	Yield of ketone (%)	Yield of hydrocarbon (%)	Ratio, Hydrocarbon : ketone
1	10	50	5 : 1
2	16	47	3 : 1
5	21	42·6	2 : 1

Owing to the nature of the solvent these experiments could not be adapted without modification for quantitative study by the carbon monoxide method. Accordingly, carbon disulphide was replaced by benzene, and toluene by anisole which when in excess is known [4] to yield almost exclusively *tert.*-butyl *p*-methoxyphenyl ketone. In dilute benzene solution *p*-*tert.*-butylanisole is no doubt also produced although this has not been isolated from the reaction mixture (see below). The different results obtained in the two methods of estimation can be discussed only qualitatively, because the conditions could not be made identical for both sets of experiments.

Inspection of Table 6 suggests that any ketone formation occurs mainly at the commencement of the reaction, since the extrapolated reaction constants decrease with increase in anisole concentration. It is also apparent that not all the differences are due to acylation; were this the case the reaction would cease in the initial stages owing to deactivation of the catalyst. The reaction with an anisole concentration of 0·063 mole/l. was repeated with a view to the isolation of the ketone : the yield of the latter was 0·045 mole/l., *i.e.*, considerably less than that indicated in Table 6. Even so, the catalyst is not deactivated to anything like the extent that would be expected were two-thirds of it combined with the ketone (compare expts. 5, 6, 7). It appears likely that ketone–catalyst combination is not instantaneous and that the titration method suffers from the defect that not all the acid is recoverable from the acid chloride–catalyst complex—no doubt a portion of this complex decomposes before the reaction can be completely quenched. Experiment " B " confirms the first conclusion. No carbon monoxide is eliminated, ketone being the

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[4] Rothstein and Saville, *J.*, 1949, 1950.

[5] *Idem*, *J.*, 1949, 1959.

sole product. Yet the yield is more than twice as great as would be expected if catalyst deactivation ran parallel to formation of the product. Olivier[6] likewise noticed that the addition of benzophenone to a reacting mixture of the benzoyl chloride–aluminium chloride complex and benzene failed to reduce the reaction velocity. On the other hand, addition of benzophenone to the above complex in crystalline condition led to the formation of a liquid which slowly deposited crystalline benzophenone–aluminium chloride. The mixture was then completely inert to benzene.

TABLE 6. *Effect of added anisole on the reactions of pivaloyl chloride in benzene.* I, Loss of CO (mole/l.) at 20·36°. II, Loss of $\mathrm{CMe_3{\cdot}COCl}$ (mole/l.) at 20·00°. $[\mathrm{CMe_3{\cdot}COCl}]$ = 0·326 mole/l. $[\mathrm{AlCl_3}]$ = 0·063 mole/l.

Expt. no.		Time (min.)						10^2k_1 (min.$^{-1}$)
		0	60	120	180	240	300	
[Anisole] = 0 mole/l.								
5, 6, 7	I †	0	0·018	0·031	0·049	0·061	0·071	0·106
1, 2, 3, 4	I	0	0·050	0·088	0·115	0·136	0·151	0·298
H1, H2	II	0·034 *	0·091	0·129	0·161	0·185	0·202	—
	Diff.	0·034	0·041	0·041	0·046	0·049	0·051	—
[Anisole] = 0·015 mole/l.								
39, 40	I	0	0·047	0·077	0·101	0·118	0·129	0·280
A1, A2	II	0·009 *	0·054	0·090	0·118	0·139	0·160	—
	Diff.	0·009	0·007	0·013	0·017	0·021	0·031	—
[Anisole] = 0·0315 mole/l.								
43	I	0	0·030	0·048	0·061	0·071	0·078	0·190
B	II	0·144 *	0·168	0·181	0·191	0·200	0·207	—
	Diff.	0·142	0·138	0·136	0·135	0·136	0·137	—
[Anisole] = 0·063 mole/l.								
41	I	0	0·024	0·040	0·050	0·057	0·062	0·168
C	II	0·142 *	0·162	0·176	0·185	0·193	0·199	—
	Diff.	0·142	0·138	0·136	0·135	0·136	0·137	—
[Anisole] = 0·126 mole/l.								
42	I	0	0·016	0·023	0·027	0·029	—	0·101
D	II	0·008 *	0·043	0·059	0·074	0·081	—	—
	Diff.	0·008	0·027	0·036	0·047	0·052	—	—
[Anisole] = solvent								
“ B ”[10]	II	0·074 *	0·098	0·110	0·120	0·128	0·133	—

* Approx. 3 min. after mixing. † $[\mathrm{AlCl_3}]$ = 0·0315 mole/l.

The Reaction with Pivalic Anhydride.—The Friedel–Crafts reaction with acid anhydrides is usually carried out by using rather more than two mols. of catalyst for each mol. of anhydride, partly because of the deactivation of the catalyst by the ketone produced and partly because one of the products is the dichloroaluminium salt of the acid :

$$(\mathrm{R{\cdot}CO})_2\mathrm{O} + 2\mathrm{AlCl_3} + \mathrm{ArH} \longrightarrow \mathrm{RArCO,AlCl_3} + \mathrm{HCl} + \mathrm{R{\cdot}CO{\cdot}O{\cdot}AlCl_2}$$

It has been stated that the acetic acid resulting from the preparation of *p*-chloro- and *p*-bromo-acetophenone from the halogenobenzenes and acetic anhydride is itself capable of affording more of the acetophenone.[7] Even at the relatively high temperature of the reaction (100°) the quoted yields are 97% and 99% based on the anhydride. Acetyl chloride can indeed be prepared from the acid and aluminium chloride, but not under the conditions described in *Org. Synth.*[8] In the experiments to be described, the yield was not greater than 98% based on the equation :

$$(\mathrm{CMe_3{\cdot}CO})_2\mathrm{O} + \mathrm{C_6H_6} \xrightarrow{\mathrm{AlCl_3}} \mathrm{CMe_3Ph} + \mathrm{CO} + \mathrm{CMe_3{\cdot}CO_2H}$$

even when the catalyst was employed in 5 : 1 excess. The results of present experiments cast doubt on the catalytic inactivity of the dichloroaluminium salt. Table 7 shows some

[6] Olivier, *Rec. Trav. chim.*, 1918, **37**, 205.
[7] *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 111.
[8] Groggins, Nagel, and Stirton, *Ind. Eng. Chem.*, 1934, **26**, 1317.

deactivation with the lower concentration of catalyst (expt. 44) but hardly any at the higher concentration (expt. 45) compared with the corresponding reactions with pivaloyl chloride ($k_1 = 0{\cdot}923$ and 3·67 min.$^{-1}$ respectively, see Table 3). The values of k_1 are considerably higher than would be expected if deactivation of the catalyst resulted from the formation dichloroaluminium salts, *i.e.*, the effective concentration of catalyst in expts. 44 and 45 would be decreased to 0·075 and 0·200 mole/l., affording calculated values of 10^2k_1 of 0·428 and 2·43 respectively, instead of those actually obtained. There was, however, a strictly linear relation between log [acid anhydride] and time for at least 50% of the reaction and a marked acceleration towards the end. The final readings for the first experiment were made at 361 min. and 500 min. and these were found to be identical; therefore the reaction had reached completion before the former time. Thus there was no indication, in spite of the final acceleration, that the pivalic acid liberated during the reaction itself underwent decomposition. The very smooth reaction is in accordance with the usual observation that acid anhydrides are preferable to acid chlorides in the Friedel–Crafts reaction. As regards the final acceleration it is of course possible that hydrogen chloride liberated during the reaction regenerated the catalyst.

TABLE 7. *Reactions between pivalic anhydride and benzene.*

Expt. no.	[$(CMe_3{\cdot}CO)_2O$] (mole/l.)	[$AlCl_3$] (mole/l.)	Method of Estimation	Temp.	10^2k_1 (min.$^{-1}$)	Total reaction (%)
—	0·0473	0·125	Titration	20·00°	0·530	87
44	0·05	0·125	Co detn.	20·36	0·700	76
45	0·05	0·250	Co ,,	20·36	3·48	98

DISCUSSION

Elimination of carbon monoxide is related to acylation, but because the concentration of the catalyst remains substantially constant, kinetically it resembles Friedel–Crafts alkylations and allied syntheses. Both acylation and alkylation are characterised by a variable order with respect to the catalyst, depending on the nature of the latter and the solvent employed. Examples of reactions dependent on the square of the catalyst concentration are the aluminium chloride-catalysed interconversion of *m*- and *p*-cresol,[9] and the methylation and ethylation of benzene with gallium trichloride.[10] On the other hand, the corresponding order for aluminium chloride in the formation of benzophenone is less than unity, that for the alkylation of benzene by 3 : 4-dichlorobenzyl chloride in nitrobenzene solution is unity. The rate-controlling step of the second reaction was shown by H. C. Brown and Grayson to be the interaction of the alkyl chloride–catalyst complex with benzene,[11] and this it will be shown should lead to first-order dependence on the catalyst concentration, as actually observed. A mechanism which elucidates the kinetics associated with the elimination of carbon monoxide, should, with the necessary changes, be equally applicable to both alkylation and acylation, and the following considerations support this view. It is reasonable to assume that the addition product of pivaloyl chloride with aluminium chloride has the same structure as that formed from other acyl halides and is therefore a 1 : 1 compound (cf. Olivier,[6] and below). This is because ketones can in fact be obtained from pivaloyl chloride. It is not implied that, because the slow step in ketone formation is the actual acylation of benzene, the correspondingly slow step in the decomposition reaction is the elimination of carbon monoxide, for there would be an accumulation of intermediate which would afford ketone even with the comparatively unreactive benzene. The diminished rate of the decomposition in the presence of quite small quantities of anisole (Table 6) is evidence that the rate-determining stage is that of complex formation. It is true that any ketone formed will eventually deactivate the catalyst but it has previously been indicated that this is a relatively slow reaction and would not be very effective initially, so that the reduced rate constants obtained by extrapolation to zero time are confirmation that a competitive reaction follows a slow one.

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[9] Baddeley, *J.*, 1943, 527.

[10] H. C. Brown, Jungh, and Smoot, Symposium on the Friedel-Crafts Reaction, Leeds, 1955.

[11] H. C. Brown and Grayson, *J. Amer. Chem. Soc.*, 1953, **75**, 6285.

Although it has recently been disputed by Korshak and N. N. Lebedev,[12, 13] it is usually considered that the acylation of the benzene nucleus is by an acyl cation R·CO$^+$. An independent cation is not necessarily involved, and the reacting entity is more probably the ion pair R·CO$^+$}AlCl$_4^-$, as in essentials was originally suggested by Boeseken,[14] by Olivier,[6] and, in 1927, more explicitly by Meerwein.[15] Olivier concluded that the rate-determining step was the bimolecular reaction between the complex (R·COCl,AlCl$_3$) and benzene. All these authors appear to have assumed the simple addition of acid halide to monomeric catalyst. In analogy with the acid chloride it seems reasonable to formulate the acid anhydride–catalyst complex as (R·CO)$_2$O$^+$,AlCl$_3^-$ though this does not exclude other structures such as (R·CO)$^+$(R·CO·O,AlCl$_3$)$^-$ which are in resonance with the first one.

Korshak and Lebedev remark on the tendency to ignore the dimeric nature of the catalyst and suggest that there is a preliminary equilibrium involving the catalyst and the solvent. A hypothesis of the kind would also account for the kinetic results described in this paper. The above authors consider that the catalyst (unsolvated) reacts as a dipolar ion, the dipole moment not being observable because of the resonance between structures such as Cl$_2$Al$^+$ ··· AlCl$_4^-$ and Cl$_4$Al$^-$ ··· AlCl$_2^+$. It must be said however, that derived structures such as (R·COCl)Al$_2$Cl$_6$ and (R·CO$^+$ ··· AlCl$_3$) AlCl$_4^-$ have in fact been proposed by various authors,[16] and it is not the case that aluminium halides always have the dimeric form known to occur in the solid or the gaseous state. Dimerisation depends both on solvent and concentration, the monomeric form existing as solvated molecules in solvents of high dielectric constant. Association of aluminium bromide, for instance, is nearly complete in benzene or carbon disulphide [6] but only slightly so in nitrobenzene. The 1 : 1 complexes of nitrobenzene with aluminium chloride and bromide are only partially associated in benzene, not more than 10% in dilute solution.[17] Similarly the dipole moment of aluminium bromide in carbon disulphide [18] at infinite dilution is zero, in benzene is $\sim 5 + 10^{-18}$, and in a mixture of benzene and nitrobenzene (one equivalent) is $\sim 9{\cdot}3 + 10^{-18}$ e.s.u. Lebedev [13] maintains that a dimeric form of the reacting complex is the acylating agent, but cryoscopic measurements again indicate that association varies with concentration, being 14% for 0·1M-solution and 87% for 0·3M-solution. Olivier [6] noted a 30% rise in the rate constant when the concentration was doubled (66% association), but this increase was negligible compared with that occurring when excess of catalyst was present. It seems probable that only the monomeric aluminium halide forms complexes with the solvent since the dipole moment of the dimeride is zero, *i.e.*, there is the equilibrium :

$$2(\mathrm{AlCl_3})^-,\mathrm{Ph{\cdot}NO_2}^+ \rightleftharpoons \mathrm{Al_2Cl_6} + 2\mathrm{Ph{\cdot}NO_2} \quad . \;\; . \;\; . \;\; . \;\; . \quad \text{(i)}$$

Lebedev [19] formulates an initial equilibrium somewhat differently and considers that only the fully ionised complex functions as the catalyst through its positive ion :

$$[(\mathrm{C_6H_5{\cdot}NO_2})_2{}^+,\mathrm{AlCl_2}^-]^+ + \mathrm{AlCl_4}^- \rightleftharpoons [(\mathrm{C_6H_5{\cdot}NO_2})_2{}^+,\mathrm{AlCl_2}^-]^+[\mathrm{AlCl_4}]^-$$

which, when solvation is neglected, is equivalent to :

$$\mathrm{AlCl_2}^+ + \mathrm{AlCl_4}^- \rightleftharpoons \mathrm{AlCl_2}^+\mathrm{AlCl_4}^- \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \quad \text{(ii)}$$

Since the undissociated complex is in the form of a dipolar ion and the reacting portion of the molecule is the solvated aluminium dichloride it does not appear that there should be much difference in the reactivity between the un-ionised and the ionised compound. Kinetically, reactions (i) and (ii) are equivalent but the advantage of the latter is that it proposes a structure equivalent to that also suggested by Lebedev for the reacting complex

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[12] Korshak and N. N. Lebedev, *Zhur. obshchei Khim.*, 1950, **20**, 266.
[13] N. N. Lebedev, *ibid.*, 1951, **21**, 1788.
[14] Boeseken, *Rec. Trav. chim.*, 1900, **19**, 19; 1901, **20**, 102.
[15] Meerwein, *Annalen*, 1927, **455**, 227.
[16] Perrier, *Compt. rend.*, 1893, **116**, 1296; *Ber.*, 1900, **33**, 815; Dilthey, *Ber.*, 1938, **71**, 1350.
[17] Ulich, *Z. phys. Chem.*, 1931, *Bodenstein Festband*, p. 423.
[18] Nespital, *ibid.*, 1932, *B*, **16**, 176.
[19] Lebedev, *Zhur. obshchei Khim.*, 1954, **24**, 664.

prepared from acid or alkyl chlorides. In general, both the monomeric and the dimeric aluminium halides can be expected to function as catalysts, though not necessarily with equal efficiency. Except in particular experiments, the composition of the solvent in the present work was kept constant; the concentration of nitrobenzene was greatly in excess of that required for 1 : 1 complex formation and consequently it can be omitted from the following considerations, *i.e.*, there are no changes in equilibrium constants due to changes in solvent composition. Since a termolecular reaction is unlikely it is usually assumed that the reaction takes place in stages, of which the second or third may be slow :

$$2\mathrm{AlCl_3} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Al_2Cl_6} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \tag{1}$$

$$\mathrm{AlCl_3} + \mathrm{R{\cdot}COCl} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (\mathrm{R{\cdot}CO^+\,AlCl_4^-}) \quad . \; . \; . \; . \; . \; . \tag{2}$$

$$\mathrm{Al_2Cl_6} + \mathrm{R{\cdot}COCl} \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} (\mathrm{R{\cdot}CO^+\,AlCl_4^-}) + \mathrm{AlCl_3} \quad . \; . \tag{2a}$$

$$(\mathrm{R{\cdot}CO^+\,AlCl_4^-}) \xrightarrow{k_5} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \tag{3}$$

Alternatively :

$$\mathrm{Al_2Cl_6} + \mathrm{R{\cdot}COCl} \underset{k_4''}{\overset{k_3''}{\rightleftharpoons}} (\mathrm{R{\cdot}CO^+\,Al_2Cl_7^-}) \quad . \; . \; . \; . \tag{2b}$$

$$(\mathrm{R{\cdot}CO^+\,Al_2Cl_7^-}) \xrightarrow{k_5'} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \tag{3a}$$

Stationary states involving the complex and the catalysts lead to the expression :

$$[\mathrm{R{\cdot}CO^+\,AlCl_4^-}] = \frac{k_3[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}]}{k_4 + k_5} + \frac{k_1k_3'[\mathrm{AlCl_3}]^2[\mathrm{R{\cdot}COCl}]}{\{k_3'[\mathrm{R{\cdot}COCl}] + k_2\}\{k_4'[\mathrm{AlCl_3}] + k_5\}}$$

Whence $\mathrm{d[CO]}/\mathrm{d}t = k_5[\mathrm{R{\cdot}CO^+\,AlCl_4^-}]$

$$= \frac{k_3k_5[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}]}{k_4 + k_5} + \frac{k_1k_3'k_5[\mathrm{AlCl_3}]^2[\mathrm{R{\cdot}COCl}]}{\{k_3'[\mathrm{R{\cdot}COCl}] + k_2\}\{k_4'[\mathrm{AlCl_3}] + k_5\}}$$

If (2) and (2*a*) are the rate-determining steps, *i.e.*, $k_5 \gg k_4$ or $k_4'[\mathrm{AlCl_3}]$, and $k_2 \gg k_3'[\mathrm{R{\cdot}COCl}]$, then

$$\mathrm{d[CO]}/\mathrm{d}t = k_3[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}] + Kk_3'[\mathrm{AlCl_3}]^2[\mathrm{R{\cdot}COCl}] \quad . \; . \; . \tag{4}$$

Thus the constant k, for the integrated equation, is given by $k = \{k_3[\mathrm{AlCl_3}] + Kk_3'[\mathrm{AlCl_3}]^2\}$, corresponding to the experimental results.

If, in the corresponding alkylation reactions (where R·CO is replaced by R), equation (3) represents the slow reaction,[18] *i.e.*, k_4 and $k_4'[\mathrm{AlCl_3}]$ are both very much greater than k_5, then the reaction becomes of the first order in the catalyst since

$$\text{rate} = \frac{k_3k_5}{k_4}[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}] + \frac{k_1k_3'k_5}{k_2k_4'}[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}]$$

$$= k_5[\mathrm{R{\cdot}COCl}][\mathrm{AlCl_3}](K' + KK''), \text{ where } K = k_1/k_2,\ K' = k_3/k_4, \text{ and } K'' = k_3'/k_4'.$$

However, in applying the foregoing equations to alkylations, cognizance must be taken of the basic strength of the halide, deactivation of the catalyst, and other factors. There seems to be no instance where the reaction is other than of the first order with respect to the halide and to the aromatic component in so far as they enter into the rate equations.

The alternative equations (2*b*) and (3*a*) assume dimeric aluminium chloride to be included in the reactive intermediate, and the rate of reaction then depends on the square of the catalyst concentration even though (3*a*) is rate-determining, since

$$\frac{\mathrm{d}[\mathrm{CO}]}{\mathrm{d}t} = \frac{k_3k_5[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}]}{(k_4 + k_5)} + \frac{k_1k_3''k_5'[\mathrm{AlCl_3}]^2[\mathrm{R{\cdot}COCl}]}{\{k_3''[\mathrm{R{\cdot}COCl}] + k_2\}(k_4'' + k_5')}$$

$$= K'k_5'[\mathrm{AlCl_3}][\mathrm{R{\cdot}COCl}] + KK'''k_5'[\mathrm{AlCl}]^2[\mathrm{R{\cdot}COCl}]$$

where $K''' = k_3''/k''$, $k_4 \gg k_5$, $k_4'' \gg k_5'$, and $k_2 \gg k_3''[\mathrm{R{\cdot}COCl}]$.

The experimental data suggest that the equilibrium constant K is small even in a solvent containing no more than 10% of nitrobenzene, and further that monomeric solvated aluminium chloride is relatively inefficient as a catalyst. The acceleration associated with increased concentrations of nitrobenzene could be partially attributed to increasing polar effects on the various equilibria, particularly those involving the monomeric and dimeric catalysts with the acid halide. A detailed study of the influence of solvent variation on reaction velocity has not yet been made for pivaloyl chloride, but alkylation of benzene by *cyclo*hexyl chloride in different mixtures of benzene and nitrobenzene has been investigated by Lebedev [19] who recorded a decrease in the reaction order as regards aluminium chloride as the proportion of nitrobenzene in the solution increased. In 85% nitrobenzene the order was 0·4; it was 1·4 in 23% solution, the extrapolated value for pure benzene being 2. Brown and Grayson [11] on the other hand observed an order of one in nearly pure nitrobenzene for alkylation by 3 : 3-dichlorobenzyl chloride. Lebedev's explanation, based on the increasing dissociation of the aluminium chloride–nitrobenzene complex and the greater catalytic activity of the dissociated than of the undissociated compound (equation ii), is unsatisfactory since these assumptions cannot explain orders ranging between the two extreme values and moreover do not envisage the effect of increasing dielectric constant on the reaction in general. He suggests that the dependence on the square root of the catalyst concentration arises from the only slightly dissociated complex, presuming that the dissociated cation is the more effective catalytically, but in that case the postulated very slow reaction catalysed by the *undissociated* complex cannot have an order greater than one. The alternative (not suggested by Lebedev) that the undissociated catalyst is the more effective and that it is largely dissociated in nitrobenzene–benzene solution provides an explanation for a two-fold, but not for a fractional, order. This second scheme is in better accord with the physical evidence, but since there is no kinetic work other than Lebedev's which deals with this point, a final decision cannot be made.

The structures of the reactive intermediates as usually formulated, namely $\mathrm{R{\cdot}CO^+\ AlCl_4^-}$ and $\mathrm{R^+\ AlCl_4^-}$, are not accepted by Lebedev who instead suggests a dimeric formula, $\{(\mathrm{RR'C{:}O})_2\mathrm{AlCl_2}\}^+\mathrm{AlCl_4}^-$ (RR′ = alkyl, aryl, or halogen).[13] His reason for doing so is that an increase of 200 Å in the maximum ultraviolet absorption of *n*-butyryl bromide is observed when it forms a complex with aluminium bromide, compared with the similar but greater increases of 700 and 400 Å shown by acetophenone and benzophenone respectively. The heats of formation of these substances with aluminium bromide show a similar relation and it was concluded that co-ordination of aluminium by oxygen had occurred. The proposed formula, however, implies a rate expression into which the halide enters as the square of its concentration, not found experimentally; but apart from this it seems almost certain that co-ordination of the type envisaged must lead to deactivation; otherwise acetophenone should afford a carbonium ion reactive in the Friedel–Crafts reaction. The lower bathochromic effect noticed with butyryl chloride may be the consequence of weaker interaction, *i.e.*, incomplete deactivation, and direct evidence of this can be obtained from Olivier's paper.[6] In the presence of a slight excess of benzoyl bromide, the rate at which benzophenone was produced was dependent on the concentration of the complex ($\mathrm{R{\cdot}COBr,AlBr_3}$) though the order is not simple. A slight molecular excess of the catalyst accelerated the reaction considerably, the increase in rate being proportional to the concentration of this excess.* The constant for the reaction could therefore be calculated

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* Similar observations by Ulich and Fragstein [20] are not comparable since these authors employed crystalline aluminium chloride and their reaction took place in a heterogeneous medium.

[20] Ulich and Fragstein, *Ber.*, 1939, **72**, 620.

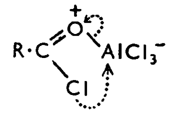
from $k = k' + k''[\mathrm{AlBr_3}]$, where k' refers to the experimentally determined constant for a given concentration of complex, and $k''[\mathrm{AlBr_3}]$ to the increment associated with the excess of catalyst. The reversibility of the reaction $\mathrm{R{\cdot}COBr + AlBr_3 \rightleftharpoons R{\cdot}COBr,AlBr_3}$ was not a factor influencing the reaction because the addition of one molecular equivalent of *m*-nitrobenzenesulphonyl chloride neither affected the rate nor led to the production of the phenyl sulphone. Thus the deactivating influence of the acid bromide evident in Table 8 which has been constructed from data selected from Olivier's paper must be due to that co-ordination to which Lebedev attributes the catalytic properties of aluminium halides.

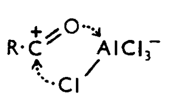
TABLE 8. *Deactivation of the benzophenone reaction by benzoyl bromide* (*Olivier* [7]).

[Ph·COBr] (mole/l.)	0·100	0·200	0·330
[AlBr$_3$] ,,	0·285	0·330	0·300
10^2k_1 (min.$^{-1}$)	5·67	4·70	0·60

The slight tendency (Table 1) for the rate constant to increase with decreasing proportions of acid halide and the more pronounced deactivation in the case of pivalic anhydride are in harmony with this view. The essential feature of all Friedel–Crafts reactions, including elimination of carbon monoxide from tertiary acid derivatives, is the carbonium ion resulting from the polarisation of the carbon–halogen link or its equivalent. The incomplete deactivation discussed above may be ascribed to resonance between the

(A)





(B)

structures (A) and (B). These would be intermediates which, though relatively inactive as acylating agents, would, in the case of tertiary and certain other acid derivatives, be inherently unstable, the rate of decomposition being dependent on the nature of R.

EXPERIMENTAL

Qualitative Reaction between Pivaloyl Chloride and Benzene in the Presence of Anisole.—A mixture of pivaloyl chloride (7·07 g., 0·326 mole/l.), anisole (1·367 g., 0·063 mole/l.), and aluminium chloride (1·513 g., 0·063 mole/l.), dissolved in a mixture of benzene (160 c.c.) and nitrobenzene (20 c.c.), was stirred for 8 hr. at 20°, then decomposed by dilute sulphuric acid. Pivalic acid (1·25 g.) was removed by dilute alkali, and the dried benzene layer fractionated. After removal of the lower-boiling constituents (benzene, anisole, *tert.*-butylbenzene, and nitrobenzene) the residual liquid, b. p. 140°/12 mm. (1·05 g., ~12% based on the unrecovered pivaloyl chloride), was identified as *p*-methoxypivalophenone. The semicarbazone, m. p. 161° (Found: C, 62·4; H, 7·4; N, 17·2. Calc. for $\mathrm{C_{13}H_{19}O_2N_3}$: C, 62·6; H, 7·6; N, 16·9%), melted 10° higher than that described by Rothstein and Saville [4] but a mixture of the two had an intermediate m. p.

Condensation of Pivaloyl Chloride with Toluene in Carbon Disulphide.—A solution of the acid chloride (6 g., 0·05 mole) in carbon disulphide was added during 30 min. to a stirred mixture of toluene, aluminium chloride (20 g., 0·15 mole), and carbon disulphide at 0°. After 15 min. the temperature was allowed to rise to 18° and stirring continued for a further 30 min. Ice and dilute sulphuric acid were added to the liquid, which was then extracted with ether; the ethereal solution was dried ($\mathrm{CaCl_2}$) and fractionated, the products being those described by Rothstein and Saville.[4] The quantity of toluene used in three experiments, the results of which are given in Table 5, were 9·2 g. (0·10 mole), 18·4 g. (0·20 mole), and 46·0 g. (0·50 mole) respectively. In each case the total volume was adjusted to 100 c.c. with carbon disulphide.

Kinetic Measurements.—Details of some typical runs were given in Part VIII. An example of a determination by the titration method where equal concentrations of acid chloride and catalyst were used, is experiment H7.

Expt. H7. Titration method. Temp. 20·0°. $[\mathrm{CMe_3{\cdot}COCl}] = [\mathrm{AlCl_3}] = 0{\cdot}10$ mole/l.

Time (min.)	0	16	46·5	90·5	180	360·5	1260
[CMe$_3$·COCl] (mole/l.)	0·090	0·077	0·066	0·055	0·037	0·022	0·017

$10^2k_1 = 0{\cdot}439$ min.$^{-1}$.

Examples of kinetic measurements in the presence of anisole are given in experiments *C* and No. 41. In each case the concentrations were: [CMe$_3$·COCl] = 0·326 mole/l., [AlCl$_3$] = [PhOMe] = 0·063 mole/l.

Expt. C. Titration method. Temp. 20·0°.

Time (min.)	[CMe$_3$·COCl] (mole/l.)	Time (min.)	[CMe$_3$·COCl] (mole/l.)	Time (min.)	[CMe$_3$·CPCl] (mole/l.)	Time (min.)	[CMe$_3$·COCl] (mole/l.)
0	0·184	90	0·156	263	0·131	500	0·110
11	0·180	169	0·142	361	0·120	1321	0·084
31	0·174						

Expt. 41. Carbon monoxide method. Temp. 20·36°.

Time (min.)	CO (mole/l.) (corr.)	[CMe$_3$·COCl] (residual) (mole/l.)	10$^2k_1$ (min.$^{-1}$)	Time (min.)	CO (mole/l.) (corr.)	[CMe$_3$·COCl] (residual) (mole/l.)	10$^2k_1$ (min.$^{-1}$)
0	0	0·326	—	180	0·0501	0·276	0·092
30	0·0139	0·312	0·146	210	0·0538	0·272	0·086
60	0·0242	0·302	0·127	240	0·0570	0·269	—
90	0·0325	0·294	0·115	270	0·0599	0·266	—
120	0·0396	0·286	0·109	300	0·0617	0·264	—
150	0·0454	0·281	0·098				

10$^2k_1$ (by extrap.) = 0·168 min.$^{-1}$.

Experiment 46 illustrates a measurement made in pure carbon tetrachloride. Neither benzene nor nitrobenzene was present.

Expt. 46. Carbon monoxide method. Temp. 20·36°. [CMe$_3$·COCl] = 0·326 mole/l. [AlCl$_3$] = 0·063 mole/l.

Time (min.)	CO (mole/l.) (corr.)	[CMe$_3$·COCl] (residual) (mole/l.)	10$^2k_1$ (min.$^{-1}$)	Time (min.)	CO (mole/l.) (corr.)	[CMe$_3$·COCl] (residual) (mole/l.)	10$^2k_1$ (min.$^{-1}$)
30	0·0150	0·311	0·157	150	0·0699	0·256	0·161
60	0·0306	0·295	0·164	180	0·0807	0·245	0·158
90	0·0448	0·281	0·164	210	0·0904	0·235	0·155
120	0·0579	0·268	0·163				

Decomposition of Pivaloyl Chloride in Pure Nitrobenzene.—The following results with initial concentrations [CMe$_3$·COCl] = 0·315 and [AlCl$_3$] = 0·063 mole/l. are illustrative.

(*a*) At 174·8 min. a solution of aluminium chloride in nitrobenzene was added, the concentrations then being [CMe$_3$·COCl] = 0·083 mole/l., [AlCl$_3$] = 0·133 mole/l.

Time (min.)	2·5	10·1	31·5	77·1	168	178·6	187	200	245
Acid reacted (%)	58	63	63	70	71	79	85	90	95

(*b*) At 58 min. the concentration of the acid chloride was raised to 0·358/mole/l.

Time (min.)	0	9·5	30	58·1	64·3	88	188
Acid reacted (%)	56	69	69	69	77	77	77

Kinetic Runs with Pivalic Anhydride.—(a) *Titration method.* One molecule of anhydride affords one molecule of carbon monoxide and one of acid. Hence, if the initial concentration of pivalic anhydride is a, and the amount transformed in time t is x, the acid found by titration $y = [2(a - x) + x]$ and the unchanged anhydride $(a - x) = (y - a)$. For this experiment, with [(CMe$_3$·CO)$_2$O] = 0·0473 mole/l. and [AlCl$_3$] = 0·125 mole/l. at 20·0°, the results were as tabulated:

Time (min.)	[CMe$_3$·CO$_2$H](y) (mole/l.)	[(CMe$_3$·CO)$_2$O] $(a - x)$ (mole/l.) *	10$^2k_1$ (min.$^{-1}$)	Time (min.)	[CMe$_3$·CO$_2$H](y) (mole/l.)	[(CMe$_3$·CO)$_2$O] $(a - x)$ (mole/l.) *	10$^2k_1$ (min.$^{-1}$)
0	0·0932	0·0459	—	137·3	0·0687	0·0214	0·496
6·2	0·0883	0·0410	—	210·4	0·0615	0·0142	0·520
18·7	0·0854	0·0381	0·590	361·4	0·0533	0·0060	0·542
54·8	0·0791	0·0318	0·526	500·0	0·0533	0·0060	—

* After the initial rapid reaction, the slope of the curve log $(a - x)$–t is given by log $(a - x) = 2·626 - 0·0023t$, whence the average value, 10$^2k_1$ = 0·530 min.$^{-1}$.

(b) *Carbon monoxide method.* One molecule of anhydride yields one molecule of carbon monoxide and thus resembles the acid chloride. Some results are recorded, for expts. 44 and 45.

Expt. 44. [(CMe$_3$·CO)$_2$O] = 0·05 mole/l. [AlCl$_3$] = 0·125 mole/l. Temp. 20·36°.

Time (min.)	[CO] (mole/l.) (corr.)	[(CMe$_3$·CO)$_2$O] (residual) (mole/l.)	10^2k_1* (min.$^{-1}$)	Time (min.)	[CO] (mole/l.) (corr.)	[(CMe$_3$·CO)$_2$O] (residual) (mole/l.)	10^2k_1 (min.$^{-1}$)
0	0	0·0500	—	105	0·0253	0·0247	0·704
15	0·0038	0·0462	—	120	0·0279	0·0221	0·708
30	0·0082	0·0418	—	135	0·0303	0·0197	0·719
45	0·0123	0·0377	0·692	150	0·0323	0·0177	0·718
60	0·0161	0·0339	0·697	165	0·0344	0·0156	0·728
75	0·0195	0·0305	0·700	180	0·0362	0·0138	0·738
90	0·0225	0·0275	0·702	195	0·0378	0·0122	0·749

* For nearly 60% of the reaction, the slope was obtained from the expression, log $(a - x) = \bar{2}{\cdot}7125 - 0{\cdot}00304t$, from which the average 10^2k_1 = 0·700 min.$^{-1}$.

Expt. 45. [(CMe$_3$·CO)$_2$O] = 0·05 mole/l. [AlCl$_3$] = 0·250 mole/l. Temp. 20·36°.

Time (min.)	[CO] (mole/l.) (corr.)	[(CMe$_3$·CO)$_2$O] (residual) (mole/l.)	10^2k_1* (min.$^{-1}$)	Time (min.)	[CO] (mole/l.) (corr.)	[(CMe$_3$·CO)$_2$O] (residual) (mole/l.)	10^2k_1 (min.$^{-1}$)
0	0	0·0500	—†	42	0·0362	0·0138	3·39
6	0·0046	0·0454	—	48	0·0389	0·0111	3·40
12	0·0123	0·0377	—	54	0·0413	0·0087	3·54
18	0·0189	0·0311	—	60	0·0431	0·0069	3·59
24	0·0244	0·0256	3·26	75	0·0466	0·0034	3·75
30	0·0289	0·0211	3·24	90	0·0489	0·0011	4·52
36	0·0329	0·0171	3·33				

† Calculated from log $(a - x) = 2{\cdot}768 - 0{\cdot}0151t$. Average 10^2k_1 = 3·48 min.$^{-1}$.

The upward drift of the rate constant with time is in obvious contrast to the gradual reduction in the case of the acid chlorides. The above equations for log $(a - x)$ were calculated by the method of least squares, using the data from 15 to 105 and from 6 to 54 min. respectively.

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