

Kinetics of Reactions of Friedel-Crafts Acylating Agents. Part II.¹ Effect of Substituents in the Acid Chloride on the Acylation of Aromatic Substrates

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The second-order rate constants for the aluminium chloride-catalysed acylation ($p\text{-XC}_6\text{H}_4\text{-COCl}$) of toluene in ethylene chloride are given at 0.0°, 20.0° for X = Me, H, and Cl and at 30.0° for X = Me and H. Similar second-order rate constants are given for PhX and RCOCl at 20.0° where X is H when R is Me, Et, and Ph and where X is Br when R is ClCH₂ and Et. The chloroacetylation of bromobenzene is shown to be independent of the concentration of an excess of acid chloride. The relative rates obtained are: toluoyl (0.2) < benzoyl (1.0) < chlorobenzoyl (2.5) with substrate toluene; benzoyl (1.0) ≪ propionyl (260) < acetyl (430) with substrate benzene and propionyl (1.0) ≪ chloroacetyl (ca. 100) with substrate bromobenzene. The oxonium complex, RCOCl₂AlCl₃, and the ion pair [RCO]⁺[AlCl₄]⁻ have previously been suggested as acylating species; these orders of reactivity may be explained by either mechanism.

IN Part I of this series¹ the 'titrimetric' and 'adiabatic' methods for measuring the rate of reactions of acylating agents were reported, using the benzylation of toluene as the model reaction. Data for several acylations of aromatic substrates in solvent ethylene chloride are now reported.

RESULTS

Acylation of Toluene.—The second-order rate constants for the acylation of toluene using *p*-toluoyl, benzoyl, and *p*-chlorobenzoyl chlorides were determined at 0.0, 20.0, and 30.0°. The results are summarized in Table 1. The effect of substituents on the rate is *p*-Me (0.2) < *p*-H (1.0) < *p*-Cl (2.5).

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¹ L. R. Pettiford, *J. Chem. Soc. (B)*, 1971, 1088.

² P. J. Sootmaekers, A. Rosschaert, and W. Janssens, *Bull. Soc. chim. belges*, 1966, **75**, 199.

With chlorobenzene as solvent Sootmaekers *et al.*² found *p*-Me (0.26) < *p*-H (1.0) < *p*-Cl (1.5).

Acylation of Benzene.—Acetylation. At first a reproducible rate constant could not be obtained; values ranging from 0.07 to 0.15 l mol⁻¹ min⁻¹ for reaction at 20.0° were found. A reproducible value of 0.112 ± 0.002 l mol⁻¹ min⁻¹ was obtained when the time between the preparation of the acetylating agent and its use in a reaction was kept constant (1½ h). If this time interval was extended to 5 h the value of *k*₂ dropped to 0.096 l mol⁻¹ min⁻¹. A value of 0.099 l mol⁻¹ min⁻¹ is obtained from an Arrhenius interpolation of the values obtained by Brown *et al.*³ at 0 and 25°.

The difficulty of obtaining reproducible results using aromatic acylating agents has been reported and explained in terms of the varying amounts of ferric chloride present as impurity in aluminium chloride.⁴ It now appears that

³ H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.

⁴ P. J. Sootmaekers, R. Roosen, and J. Verhulst, *Bull. Soc. chim. belges*, 1962, **71**, 446.

for an acetylating agent the age of the reagent also influences the rate of reaction.

Propionylation. The second-order rate constant obtained for this reaction was $0.067 \pm 0.003 \text{ l mol}^{-1} \text{ min}^{-1}$ at 20.0° ; the rate relative to that for acetylation is 0.60. The latter value is in good agreement with that (0.62) obtained by Smeets and Verhulst⁵ with bromobenzene or chlorobenzene as reactant and solvent.

Benzoylation. The second-order rate constant obtained $0.026 \pm 0.001 \times 10^{-2}$ at $20.0^\circ \text{ l mol}^{-1} \text{ min}^{-1}$; consequently the relative rate of acetylation to benzoylation is 430. This is in line with reported relative rates of 1370 at 0° ⁶ and 300 (approx)^{*} at 25° .³

Acylation of Bromobenzene.—Chloroacetylation. The second-order rate constant at 20.0° was found to be $0.054 \pm 0.002 \text{ l mol}^{-1} \text{ min}^{-1}$ in one series of experiments but in a further series at a later date a value of $0.062 \pm 0.002 \text{ l mol}^{-1} \text{ min}^{-1}$ was obtained. The acylating agents in the two

presence of uncombined acid chloride.^{7,3} Similar results have now been obtained for the chloroacetylation of bromobenzene. The same mechanism would, therefore, explain the acylations of all three aromatic substrates.

Two mechanisms have been proposed;⁸ the first involves the oxonium complex $\text{RCCl}:\overset{+}{\text{O}}-\overset{-}{\text{AlCl}}_3$ as the acylating agent while in the second the ion-pair $[\text{RCO}]^+[\text{AlCl}_4]^-$ is the acylating species. Slootmaekers and his co-workers, who have extensively studied the effects of substituents on the reactivity of aromatic acid chloride as acylating agent, have concluded that a third mechanism, which is second-order in acylating agent, is also involved.⁹ They suggest that either the acylating agent may also react with a complex of acylating agent and aromatic hydrocarbon or that a dimeric species of the acylating agent is involved.

TABLE 1
Acylation of toluene

Temp.	Acid chloride	Molarity of ArCOCl(M)	Molarity of toluene(M)	Molarity of excess of acid chloride(M)	$k_2 \times 10^2$ ($\text{l mol}^{-1} \text{ min}^{-1}$)	$\frac{k_2(p-X)}{k_2(p-H)}$
0.0°	Benzoyl	0.142	0.271	0.05	0.74 ± 0.03	1.0
20.0	Benzoyl	0.124	0.271	0.27	3.6 ± 0.1	1.0
30.0	Benzoyl	0.129	0.271	0.05	8.5 ± 0.2	1.0
0.0	<i>p</i> -Toluoyl	0.123	0.271	0.04	0.12 ± 0.01	0.16
20.0	<i>p</i> -Toluoyl	0.133	0.271	0.06	0.70 ± 0.03	0.19
30.0	<i>p</i> -Toluoyl	0.104	0.268	0.08	1.5 ± 0.05	0.18
0.0	<i>p</i> -Chlorobenzoyl	0.151	0.271	0.04	1.7 ± 0.1	2.3
21.5	<i>p</i> -Chlorobenzoyl	0.136	0.274	0.03	10.0	2.7

series were coloured yellow and red respectively: a change in rate constant with the colour of the acylating agent was also observed in the benzoylation of toluene.¹

In the second series the concentration of free acid chloride was varied from 0.04 through 0.08 and 0.10 to 0.19M with no change in the rate constant.

The second-order rate constants recorded above were obtained under conditions which provided pseudo-first-order kinetics. That this reaction is second-order was confirmed by an experiment using molarities of chloroacetylating agent and bromobenzene of 0.120 and 0.289M respectively: a value for k_2 of $0.065 \text{ l mol}^{-1} \text{ min}^{-1}$ was obtained.

Propionylation. The rate of this reaction is only two to three times that of decomposition of propionylating agent and a blank experiment was employed to enable a correction to be made for decomposition. A value of *ca.* $5.5 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$ was obtained for k_2 at 20.0° ; the rate of propionylation of bromobenzene is, therefore *ca.*, 1/100th that for chloroacetylation.

DISCUSSION

The benzoylation of toluene and the acetylation of benzene in solvent ethylene dichloride exhibit second-order kinetics and the rate constant is unaffected by the

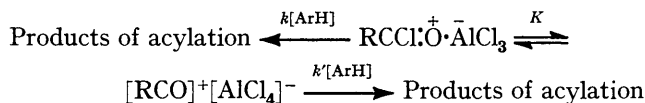
* Brown *et al.* use '500-fold' presumably because of the difficulty specifying a relative rate based on different concentrations of acylating agent. The rel. rate acetylation (0.2M)/benzoylation (0.3M) is 286.

⁵ F. Smeets and J. Verhulst, *Bull. Soc. chim. belges*, 1954, **63**, 439.

⁶ P. H. Gore, J. A. Hoskins, and S. Thorburn, *J. Chem. Soc. (B)*, 1970, 1343.

This third-order mechanism decreases in importance with decreasing basicity of both the aromatic hydrocarbon and the solvent. The simple overall second-order kinetics now observed for the acylation of toluene, benzene, and bromobenzene in ethylene dichloride solution indicate that in these reactions only the route which is first-order with respect to acylating agent is involved.

Slootmaekers *et al.* initially² held the view that the ion-pair $[\text{RCO}]^+[\text{AlCl}_4]^-$ is the acylating agent but subsequently concluded that the oxonium complex could also be the agent.¹⁰ The orders of reactivity of acid chlorides given above do not distinguish between the two mechanisms since, in the reaction scheme below, substituents may have a larger effect on the rate constant k' than on the equilibrium constant K .



The activation parameters calculated for aromatic acylating agents are given in Table 2. As shown, they

⁷ F. R. Jensen, G. Marino, and H. C. Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3303.

⁸ F. R. Jensen and G. Goldman in 'Friedel-Crafts and Related Reactions,' ed. G. Olah, Interscience, New York, 1964, vol. III, pt. 2.

⁹ G. Hoornaert and P. J. Slootmaekers, *Bull. Soc. chim. belges*, 1968, **77**, 295; 1969, **78**, 253; 257.

¹⁰ R. Verbeest and P. J. Slootmaekers, *Bull. Soc. chim. belges*, 1968, **77**, 287.

are in good accord with those of Brown *et al.*; the small difference may be due to the different initial concentrations. A similar change in enthalpy of activation and entropy of activation with concentration is shown by the parameters obtained by Sloomackers *et al.* using chlorobenzene as solvent (see Table 2). The similarity between the values for enthalpy of activation and entropy of activation obtained in ethylene chloride, benzoyl chloride, and chlorobenzene as solvents indicates that effectively the same mechanism is involved.

EXPERIMENTAL

Materials.—The aluminium chloride, ethylene chloride, and toluene used were as described in Part I.¹ Acid chlorides

0.024 mol. Zero time was recorded as the excess of acid chloride was added. Acetylating agent was 52% decomposed in 24 h, propionylating agent 15% in 49 h, and chloroacetylating agent was unchanged after 68 h. Except where indicated these decay rates are too slow to affect the reactions studied.

Acetylation of Benzene.—Immediately after preparation of the acetylating agent 50.0 ml were placed in an 'adiabatic' apparatus (*ca.* 100-ml capacity) and left for 1½ h before benzene (5.00 ml; 1.02M) was added. The acetylating agent was 0.05M and contained excess of acid chloride (0.13M).

Propionylation of Benzene.—Acetylation was repeated. The molarity of propionylating agent was 0.05M and that of excess acid chloride 0.16M.

TABLE 2

Activation parameters for the acylation of toluene

Acid chloride	Energy of activation (E_a) (kcal mol ⁻¹)	Log A (s ⁻¹)	Enthalpy of activation (ΔH^\ddagger) (kcal mol ⁻¹)	Entropy of activation (ΔS^\ddagger) (cal mol ⁻¹ deg ⁻¹)
Benzoyl	13.4	6.79	12.8	-29.3
<i>p</i> -Toluoyl	13.9	6.37	13.3	-31.1
<i>p</i> -Chlorobenzoyl	13.2	7.00	12.6	-26.5
Benzoyl (0.10M) ^a	13.9	7.08	13.3	-28.1
Benzoyl (0.10M) ^b	13.3	7.49	12.6	-26.7
Benzoyl (0.19M) ^c			13.5	-28.8
<i>p</i> -Toluoyl (0.19M) ^c			14.3	-28.7
Benzoyl (0.11M) ^c			14.2	-26.7
<i>p</i> -Toluoyl (0.11M) ^c			15.0	-26.5

^a Solvent ethylene chloride.⁷ ^b Solvent benzoyl chloride.⁷ ^c Solvent chlorobenzene.²

were either B.D.H. reagent grade re-distilled to 1° boiling range or prepared from the acid and thionyl chloride or phosphorus trichloride. Benzene (AnalaR grade) was re-distilled from sodium. Bromobenzene (reagent grade) was re-distilled after it had been set aside over calcium chloride.

Preparation of the Acylating Agents.—These reagents were prepared by Method A.¹ The quantities of reagents used are defined: aluminium chloride (j g), ethylene chloride (i) for washing aluminium chloride (k ml) and (ii) as solvent (l ml) and acid chloride (i) added initially (m ml) and (ii) subsequently added after decantation from excess aluminium chloride (n ml). Values of j , k , l , m , and n are given in Table 3.

Acylation of Toluene.—The rates were determined by the 'titrimetric method' except for *p*-chlorobenzoylation at *ca.* 20.0° for which the 'adiabatic method' was used. Under second-order conditions T_∞ cannot be calculated and therefore T_∞ and T_0 were estimated by extrapolation of the corrected temperature curve; a plot of $\log \{[(T_\infty - T_0) / (a/b - 1)] / (T_\infty - T_0)\} + 1$ against time is a straight line with slope $k_2(a - b)/2.3$. The initial temperature was 19.9° and the maximum temperature reached was 22.1°. The average reaction temperature assumed for calculation was 21.5°.

Stability of Aliphatic Acylating Agents.—The half-life of an acetylating agent has been given¹¹ as 3 h at 14° but other workers have reported satisfactory second-order kinetics.³ Consequently, the concentrations of acylating agents from acetyl, propionyl, and chloroacetyl chlorides were measured at various times using mesitylene in the 'titrimetric method'. The acylating agents were prepared by Method A;¹ the relevant values of j , k , l , m , and n (see above) are 0.016 mol, nil, 150.0, 0.012 mol, and

Benzoylation of Benzene.—The rate was measured by the 'titrimetric method' using mesitylene. Benzene (2.30 ml) was added to benzoylating agent (91.0 ml). Reaction

TABLE 3

Acid chloride	Substrate	j	k	l	m	n
Benzoyl	Toluene	4.5	20.0	150.0	2.00	1.00 ^a
Benzoyl	Toluene	4.0	20.0	100.0	1.20	3.80
Benzoyl	Toluene	4.0	20.0	125.0	1.50	1.00 ^a
Toluoyl	Toluene	4.0	20.0	125.0	2.00	1.00 ^a
Toluoyl	Toluene	4.0	20.0	125.0	1.75	1.00 ^a
Toluoyl	Toluene	4.0	20.0	125.0	2.00	1.00 ^a
<i>p</i> -Chlorobenzoyl	Toluene	4.5	20.0	125.0	2.00	1.00 ^a
<i>p</i> -Chlorobenzoyl	Toluene	4.0	20.0	125.0	1.75	1.00
Acetyl	Benzene	0.7	Nil	51.0	0.25	0.50
Propionyl	Benzene	0.7	Nil	51.0	0.37	0.72
Benzoyl	Benzene	4.0	20.0	125.0	1.42	1.30
Chloroacetyl	Bromo- benzene	1.6	Nil	113.0	0.55	0.55, 0.94, 1.10, ^b 3.04
Chloroacetyl ^c	Bromo- benzene	4.0	20.0	125.0	1.00	0.79
Propionyl	Bromo- benzene	4.0	10.0	100.0	1.00	1.00

^a Added to 100.0 ml. ^b Used in the first series of experiments. ^c The second-order experiment.

molarities of benzene, benzoylating agent and excess of benzoyl chloride were 0.277, 0.123, and 0.05M, respectively. The reaction was followed to 58% (10 days).

Chloroacetylation of Bromobenzene.—In the pseudo-first-order experiments 5.00 ml of bromobenzene (1.07M) was added to 50.0 ml of chloroacetylating agent (0.06M); in the second-order experiment 2.20 ml (0.289M) was added to 70.5 ml (0.120M).

¹¹ M. M. I. Arab, M.Sc. Thesis, Cairo, 1966.

Propionylation of Bromobenzene.—Bromobenzene (2.10 ml; 0.278M) was added to 75.0 ml of propionylating reagent (see Table 3) and the remainder was used as a 'blank'. Consumption of the propionylating agent was measured by the 'titrimetric method' using mesitylene. The initial molarity of propionylating agent was 0.110M. After 533 and 1323 min it was 0.097 and 0.080M while the concentration of the 'blank' had fallen by 0.05 and 0.09M

respectively. Using corrected values for the concentration of propionylating agent of 0.102 and 0.089M the values obtained for k_2 at 20.0° are 5.2 and $5.6 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$ respectively.

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