The Friedel–Crafts Acetylation of Naphthalene in 1,2-Dichloroethane Solution. Kinetics and Mechanism

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The Friedel–Crafts acetylation of naphthalene, using acetyl chloride and aluminium chloride in 1,2-dichloroethane solution, has been studied kinetically. The α/β isomer ratio changes as a function of concentration of reactants, and time, *e.g.* from an initial 4–5 to a final 0.7. The results point to a different dependence for the two positions on the concentration of acylating reagent, $AcCl,AlCl_3$, being second-order in this reagent for the α-reaction and first-order for the β-reaction. The rate of the α-reaction is impeded by the presence of free acetyl chloride, whilst the β-reaction is unaffected. The latter reaction exhibits activation parameters in the expected range, $\Delta H^{\ddagger}$ = *ca.* 48 kJ mol^{-1} and $\Delta S^{\ddagger}$ = *ca.* −99 J K^{-1} mol^{-1}, whereas for the α-reaction $\Delta H^{\ddagger}$ = *ca.* 21 kJ mol^{-1} and $\Delta S^{\ddagger}$ = *ca.* −160 J K^{-1} mol^{-1} are both very low. Competitive and non-competitive kinetic hydrogen isotope experiments were carried out using [$^2H_8$]naphthalene. The mechanism for β-naphthyl acetylation is believed to involve a two-stage process, the second (loss of proton) being rate-limiting. The α-acetylation is believed to proceed through a σ-complex, from which elimination of HCl to give products is prevented for steric reasons; the reaction instead proceeds through a second σ-complex, decomposition of which is usually at least partly rate-limiting.

Although the Friedel–Crafts acetylation of naphthalene is now a century old,[1] meaningful quantitative work on this reaction has been scarce. No kinetic investigation of the acetylation of naphthalene has been published, except for some rather bizarre results obtained in a reaction where the acylating agent was believed to be the Illari acetylating reagent, CH_2=C(Cl)O$AlCl_2$.[2]

Reasons for the absence of any published accounts of the kinetics of Friedel–Crafts acetylations generally, using the classical system acetyl chloride/aluminium chloride, are not hard to find. The reaction is fast; therefore very dilute solutions of reagents need to be used, which worsens the problems associated with trace amounts of adventitious water. Moreover, if the hydrogen chloride gas produced is allowed to escape from the reaction medium, it will entrain quantities of the acetyl chloride reagent, especially if used in excess. If the reaction is moderated by cooling crystallisation of aluminium chloride complexes becomes a problem.

The Friedel–Crafts acetylation of naphthalene is of particular interest, since it was shown[4] that the α/β-isomer ratio was concentration-dependent. The results obtained for 1,2-dichloroethane solution pointed to a duality of mechanism, in that β-acetylation is first-order in acylating reagent ($AcCl,AlCl_3$), whereas α-acetylation is second-order in the acylating reagent.

This paper describes kinetic studies of the Friedel–Crafts acetylation of naphthalene in 1,2-dichloroethane solution, the special difficulties of the system referred to above having been satisfactorily overcome.

Discussion

Experimental Procedure.—A technique was developed for the present system (see Experimental section), whereby, for the preparation of the reagents and solutions, exposure to a moist atmosphere was avoided altogether, and all prior operations were carried out in a dry nitrogen atmosphere. The reaction vessel was a 3-neck flask almost completely immersed in a constant temperature bath (usually 0 °C). The sampling technique allowed aliquots to be withdrawn at rapid intervals (down to 10 s), without *either* the sample taken *or* the reaction solution itself being exposed to the laboratory atmosphere. Analysis was carried out on the aliquots: after quenching with water or diethyl ether, and a simple work-up, the amounts of α-(**Ib**) and β-(**Ic**) acetylnaphthalenes were determined (normally within ±0.5–1.0%), relative to the quantity of a marker substance (usually an *n*-alkane), permitting the absolute yields of ketones to be calculated.

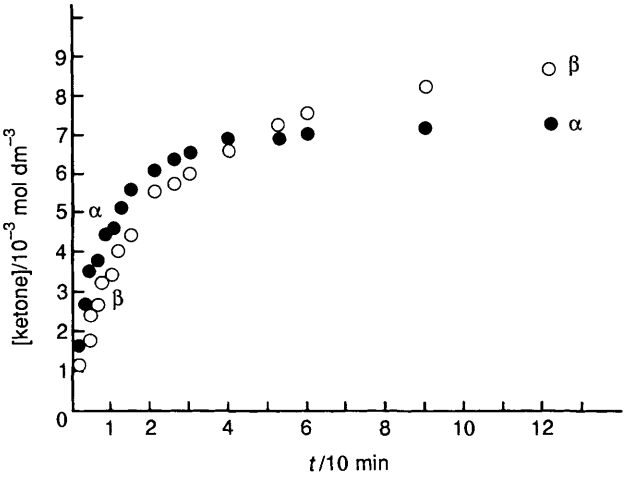


Fig. 1 Formation of α-ketone (●) and β-ketone (○), as a function of time, in a typical Friedel–Crafts acetylation of naphthalene in 1,2-dichloroethane solution

Calculations.—A typical set of percentage isomer data is presented in Fig. 1. In order to obtain k_α and k_β, various possibilities in respect of the kinetic equations which could reasonably apply to the component reactions were explored. The only set of equations which gave satisfactory results, *i.e.* internal consistency and replicability, involved eqns. (1) and (2).

$$\text{Rate}_\alpha = k_\alpha[\text{naphthalene}][AcCl,AlCl_3]^2 \quad (1)$$

$$\text{Rate}_\beta = k_\beta[\text{naphthalene}][AcCl,AlCl_3] \quad (2)$$

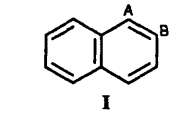
These kinetic expressions represent different dependences for the two naphthyl positions on reactant concentrations. This confirms our earlier deduction,[4] based on analyses of per-

centages of isomer formation, that these kinetic expressions applied to Friedel–Crafts acetylations of naphthalene in 1,2-dichloroethane solution.

Computer programs were developed for the solution of the kinetic expressions for the above two competing reactions. When applied to a set of data of concentrations *vs.* time, these yielded single rate coefficients, third-order (k_α) for the reaction at the 1-position, and second-order (k_β) for the reaction at the 2-position of naphthalene, respectively. Analysis showed that a contribution of *ca.* 5% of a second-order component to the reaction at the 1-position represents the upper limit, whereas that for a third-order component to the reaction at the 2-position is well below a 5% limit. In the absence of any evidence to the contrary, it is understood that in the system under consideration one is dealing with (essentially) pure third-order and pure second-order component reactions. In the one comparable case in the literature, that dealing with the Friedel–Crafts benzoylation of naphthalene,[5,6] it was found that the reaction at the 1-position involves a significant second-order component.

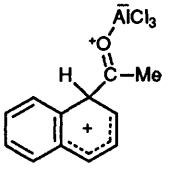
Results

A typical plot of yields of the two isomers, α(**Ib**) and β(**Ic**) acetylnaphthalanes, *vs.* time is given in Fig. 1. The initial formation of the α-isomer is rapid but its curve soon flattens out, whilst that of the β-isomer climbs more steadily and overtakes the α-isomer, in the example given after *ca.* 4 min. Formation of the α-isomer is virtually complete after 10 min, but the β-isomer continues to increase for 1 h; there is little change thereafter. The total yield of acetyl isomers was usually 90–95%, and typically the shortfall in yield was *ca.* 0.004 mol dm^{-3}. Since monoacetylnaphthalenes have been shown to be inert towards further acetylation under such mild conditions,[7] formation of diketones could be discounted as a cause. Since rates of protiodeacylation of these ketones are known to be negligibly small,[8] the incomplete conversion to monoketones is not the consequence of an equilibrium being attained. Since, moreover, there is no evidence that the isomers can be interconverted under classical Friedel–Crafts conditions, the possibility (which might be suggested by the shapes of the curves in Fig. 1) of kinetic *vs.* thermodynamic control (*viz.* of a reversible substitution akin to the sulphonation of naphthalene) can be discounted.

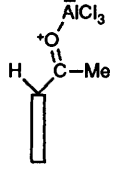


I

a; A = B = H
b; A = Ac, B = H
c; A = H, B = Ac



IIa



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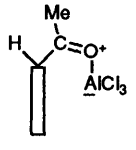

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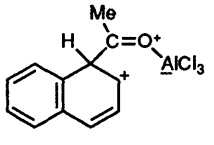
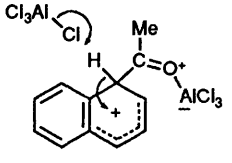


IIIb



IV

This leaves the removal of a reagent in a side reaction as the probable cause of the shortfall in overall yield. Since the latter was observed even in the presence of an excess of acetyl chloride or of naphthalene, the reactant involved is aluminium chloride. It is probable that complexation of $AlCl_3$ with water is responsible. By assuming that the initial concentration of the acylating complex equals the final total concentration of product ketones, one obtains rate coefficients which are internally consistent within a given run, and which show very satisfactory correlation between runs.

Variations in Rate Coefficients, k_α *and* k_β.—Table 1 shows a few representative data, giving rate coefficients calculated for different initial concentrations of reactants. Experiments (*a*) and (*b*) show satisfactory correspondence in replicate runs. Due to the experimental technique used, it was difficult to vary the concentrations of reactants one at a time. However, data given in Table 1 show that for reasonably constant concentrations of the acylating reagent, [AcCl,$AlCl_3$] = [R] = *ca.* 0.035 mol dm^{-3}, and of excess of acetyl chloride = *ca.* 0.043 mol dm^{-3}, a 6-fold increase in concentration of naphthalene ([N]) [experiments (*a*)–(*f*)] gives rate coefficients, k_α and k_β, which vary little. For a different range of initial concentrations of reactants [experiments (*g*)–(*m*)], values of the rate coefficients again show little variation; however, whilst the derived values of k_β change little, values of k_α are seen to be some 45% higher at the higher [R] = *ca.* 0.035 mol dm^{-3} and lower [$AcCl_f$] = *ca.* 0.043 mol dm^{-3}. Therefore, the data indicate that the β-reaction is first-order in naphthalene, and that it is independent of the concentration of free acetyl chloride. The data further indicate that the α-reaction is also first-order in naphthalene, but that it is dependent also on the concentration of free acetyl chloride, [$AcCl_f$].

The effect on rate coefficients of changing the concentration of free acetyl chloride, [$AcCl_f$], is isolated in experiments given in Table 2, *i.e.* concentrations of acylating reagent (R) are kept virtually constant. Changes in free acetyl chloride concentration, as above, cause no variation in the magnitude of the rate coefficient, k_β. In contrast, as [$AcCl_f$] is increased there is a significant *decrease* in the magnitude of k_α, such a decrease being relatively small at low concentrations, and quite large at relatively high concentrations, of excess acetyl chloride. This is in keeping with the data given in Table 1 for two such sets of concentrations. An inverse concentration effect on the magnitude of the rate coefficient k_α implies that free acetyl chloride is a reactant, but that the term [$AcCl_f$] will be found in the *denominator* of the appropriate rate expression.

As will be shown below, plots of $1/k_\alpha$ (or k_β/k_α) *vs.* [$AcCl_f$] give satisfactory straight lines (*cf.* Fig. 2). This relationship can be used to assess the kinetic dependence of the α-acetylation on the acylating reagent (R). For a mean value of [R] = 0.016 mol dm^{-3} [using data of runs (*g*)–(*l*) of Table 1, and three further runs], the mean value of k_α = 2.12 dm^6 mol^{-2} s^{-1} (s.d. 0.25) at the mean [$AcCl_f$] = 0.0622 mol dm^{-3} (s.d. 0.0022). This value of k_α can then be compared with the corresponding value at the higher [R] = 0.36 mol dm^{-3} (Table 2), obtained by interpolation in the graph (Fig. 2) for the value of [$AcCl_f$] = 0.0622 mol dm^{-3} to give k_α = 2.38 dm^6 mol^{-1} s^{-1}. This value is the same as that at the lower [R], within experimental error. Another method used, which gave the same result, was to observe the values of k_α as individual points at the beginning, and at the end, of a run; this was also confirmed computationally.

The kinetic dependence of 2-naphthyl acetylation is quite straightforward: k_β is independent of [R], as seen from its

Table 1 Effect of concentrations of reactants on rate coefficients

Expt.	[N]/mol dm^{-3}	[AcCl,AlCl$_3$]/mol dm^{-3}	[AcCl$_f$]/mol dm^{-3}	(k_α/k_β)/dm^3 mol^{-1}	k_α/dm^6 mol^{-2} s^{-1}	k_β/dm^3 mol^{-1} s^{-1}
(*a*)	0.0392	0.0340	0.0490	84.9	2.69	0.0317
(*b*)	0.0393	0.0343	0.0484	86.0	2.77	0.0322
(*c*)	0.0745	0.0346	0.0401	91.9	2.70	0.0294
(*d*)	0.0780	0.0364	0.0418	88.8	2.64	0.0308
(*e*)	0.0955	0.0343	0.0362	106	3.32	0.0315
(*f*)	0.2340	0.0350	0.0442	94.6	2.81	0.0298
Mean		0.0348	0.0433		2.82	0.0309
s.d.					0.23	0.0010
(*g*)	0.0196	0.0153	0.0632	64.3	1.89	0.0293
(*h*)	0.0201	0.0132	0.0653	65.7	1.94	0.0295
(*j*)	0.0209	0.0178	0.0602	65.0	1.91	0.0294
(*k*)	0.0358	0.0168	0.0614	63.9	1.79	0.0281
(*l*)	0.0424	0.0130	0.0647	73.9	2.27	0.0308
(*m*)	0.0790	0.0198	0.0595	71.8	1.86	0.0258
Mean		0.0160	0.0624		1.94	0.0288
s.d.					0.15	0.0016

Table 2 Effect of free acetyl chloride on rate coefficients

[N]/mol dm^{-3}	[AcCl,AlCl$_3$]/mol dm^{-3}	[AcCl$_f$]/mol dm^{-3}	(k_β/k_α)/10^{-3} mol dm^3	k_α/dm^6 mol^{-2} s^{-1}	k_β/dm^3 mol^{-1} s^{-1}
0.0804	0.0376	0.0130	8.26	3.92	0.0327
0.0784	0.0329	0.0220	8.61	3.40	0.0293
0.0955	0.0343	0.0362	9.48	3.32	0.0315
0.0745	0.0346	0.0403	10.9	2.70	0.0294
0.0780	0.0364	0.0418	11.3	2.74	0.0308
0.0793	0.0379	0.120	17.5	1.85	0.0323
0.0772	0.0357	0.271	30.7	0.950	0.0289
Mean					0.0307
s.d.					0.0014

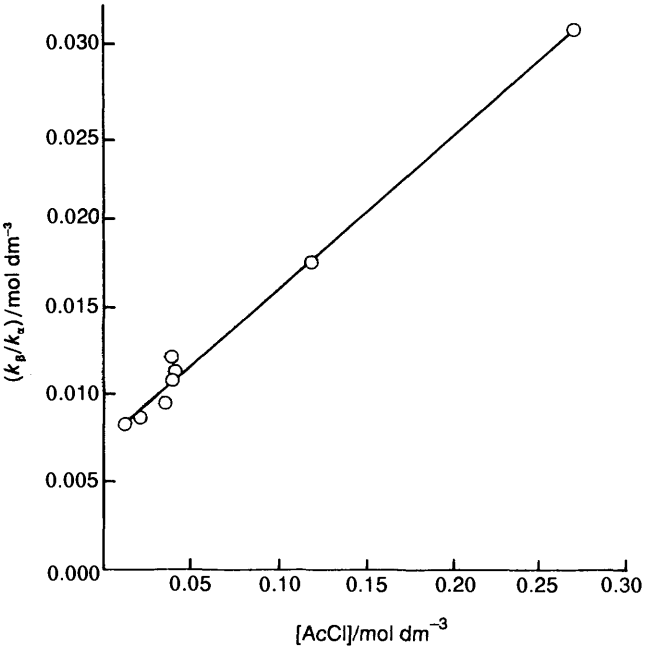


Fig. 2 Ratio of rate coefficients, k_β/k_α, as a function of concentration of free acetyl chloride, in 1,2-dichloroethane solution at 0 °C. Slope = 0.0865 ± 0.0077; intercept = 0.007 28 ± 0.000 83; correlation coefficient = 0.9961.

constancy; for 20 runs at [R] = 0.015 or 0.035 mol dm^{-3}, k_β = 0.0305 ± 0.0006 dm^3 mol^{-1} s^{-1} (98% confidence limits; standard error of mean = 1.4%).

Effect of Temperature.—In order to see if the competing acetylation reactions are 'well-behaved' and to obtain activation parameters, the effect of temperature on the rates was studied, within the practical limits imposed by the system. The results are summarised in Table 3, for one set of reaction conditions, within the temperature range −23 °C to +20 °C. The Arrhenius plot for the reaction at the 2-naphthyl position is remarkably well correlated, but the plot for the reaction at the 1-naphthyl position is no more than moderate in precision, but (see above) this is not due to accumulation of errors. The enthalpies of activation, $\Delta H^\ddagger$, are seen to be rather low for both reactions, but especially so for the α-reaction. The entropy of activation (β-position), calculated for 0 °C, is −99 J K^{-1} mol^{-1}, comparable in magnitude to that (−112 to −118 J K^{-1} mol^{-1}) found[9] for the aluminium chloride-catalysed acetylation or benzoylation of benzene or toluene, under a variety of conditions. The entropy of activation for the 1-naphthyl reaction is considerably lower, by *ca.* 65 J K^{-1} mol^{-1}. This is very similar to the corresponding difference (*ca.* 50 J K^{-1} mol^{-1}) found[5] for naphthalene benzoylations. These differences in the activation parameters strongly suggest differences in the reaction mechanisms at the two naphthyl positions: this will be discussed below.

Kinetic Hydrogen Isotope Effect.—To study the effect of replacing hydrogen by deuterium in the substrate naphthalene, two types of experiments were conducted.

Non-competitive experiments. Two kinetic runs were performed on normal naphthalene, and two runs, under precisely the same conditions, on [$^2H_8$]naphthalene; the results are summarised in Table 4. At the 1-naphthyl position there is a

Table 3 (*a*) Effect of temperature on rate coefficients k_α and k_β, and (*b*) derived activation parameters[a]

(*a*) T/K	k_α/dm^6 mol^{-2} s^{-1}	k_β/dm^3 mol^{-1} s^{-1}
250.15	0.731	0.003 65
259.65	1.38	0.008 77
273.15	1.79	0.028 1
282.15	2.64	0.056 4
293.15	4.13	0.124

(*b*)	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1} [b]	$\Delta G^\ddagger$/kJ mol^{-1} [b]	Correlation coefficient	k[c]
1-naphthyl	20.7 ± 6.7	−163 ± 25	65.1 ± 13.6	0.987 4	1.98[d]
2-naphthyl	47.8 ± 0.5	−98.9 ± 1.9	74.8 ± 1.0	0.999 98	0.027 8[e]

[a] [N] = 0.0360 mol dm^{-3}; [AcCl,AlCl$_3$] = 0.0197 mol dm^{-3}; [AcCl$_f$] = 0.0780 mol dm^{-3}. [b] Calculated at 0 °C. [c] Interpolated at 0 °C. [d] Units: dm^6 mol^{-2} s^{-1}. [e] Units: dm^3 mol^{-1} s^{-1}.

Table 4 Results from non-competitive isotope effect experiments[a,b]

Substrate	k_α/dm^6 mol^{-2} s^{-1}	k_β/dm^3 mol^{-1} s^{-1}	(k_α/k_β)/dm^3 mol^{-1}
Naphthalene	2.57	0.031 3	80.6
Naphthalene	2.27	0.030 8	73.9
[$^2H_8$]Naphthalene	1.49	0.007 71	194
[$^2H_8$]Naphthalene	1.38	0.006 88	201

[a] Kinetic hydrogen isotope effect: α-position = 1.68 (s.d. 0.12); β-position = 4.25 (s.d. 0.25). [b] [substrate] = *ca.* 0.035 mol dm^{-3}, [AcCl,AlCl$_3$] = 0.0195 mol dm^{-3}, [AcCl$_f$] = 0.078 mol dm^{-3}.

Table 5 Summary of kinetic hydrogen isotope effects using competitive conditions

			Isotope effect, k_H/k_D			
			1-naphthyl posn.		2-naphthyl posn.	
Expt.	[AcCl,AlCl$_3$] mol dm^{-3}	[AcCl$_f$] mol dm^{-3}	uncorr.	corr.[a]	uncorr.	corr.[a]
(*n*)	0.0041	0.0942	2.17	2.22	4.11	4.35
(*p*)	0.0337	trace	1.09[b]	1.09[b]	5.07[b]	5.39[b]
(*q*)	0.0168	0.0725	1.236	1.243	5.04	5.40
(*r*)	0.0174	0.0751	1.70	1.61	5.01	5.35

[a] Corrected for incomplete deuteriation. [b] Subject to some error due to isotopic scrambling.

significant kinetic hydrogen isotope effect, whilst at the 2-naphthyl position the effect is uncommonly large. The only comparable kinetic hydrogen isotope effects for Friedel–Crafts acetylations, giving ratios, k_H/k_D = *ca.* 2, have been obtained for benzene and toluene in nitrosolvents.[10]

Competitive experiments. In this series of experiments a mixture of naphthalene and [$^2H_8$]naphthalene was allowed to compete for a small concentration of acetylating reagent, and their relative reactivities were determined, after separation by GC of the two (1- and 2-naphthyl) ketones formed, by mass spectroscopic analysis (see Experimental section). Since the substrates were employed in large excess, the kinetic isotope effect is readily calculated using eqn. (3). In eqn. (3) the

$$\frac{k_H}{k_D} = \frac{[\text{acetylnaphthalene}][[^2H_8]\text{naphthalene}]}{[[^2H_7]\text{acetylnaphthalene}][\text{naphthalene}]} \quad (3)$$

naphthalene terms are average values within the run, but because of the large excess of substrates used these values will be close to the initial concentrations. The ratios of acetylnaphthalene to [$^2H_7$]acetylnaphthalene were obtained from peak heights of the parent ions, as described below. Four competitive experiments were carried out, one [Table 5 (*n*)] under conditions where 2-acetylnaphthalene is the predominant product, one [(*p*)] under conditions favouring the 1-isomer, and two [(*q*),(*r*)] conducted under intermediate conditions similar to those employed in the non-competitive runs (Table 4).

The large kinetic isotope effect at the 2-naphthyl position was unexpected, because it implies that in a two-stage substitution process *via* a Wheland intermediate it is proton-abstraction which is rate-limiting. If this proton transfer is intermolecular, then the base responsible should appear in the rate equation. However, the most likely candidate for the role of proton acceptor, *viz.* acetyl chloride, does not change the rate of the reaction, when added in excess. This leads to the conclusion that proton transfer must here be *intramolecular*. This is further discussed below.

For the 1-naphthyl position, in the event of free acetyl chloride being absent [Table 5 (*p*)], the kinetic hydrogen isotope effect is close to unity; the remaining experiments of Table 5 give values which are somewhat larger, and suggest that proton transfer in these reactions is at least partially rate-limiting. The mechanistic implications of these results are also discussed below.

The Acetylation Mechanisms.—The Friedel–Crafts acetylation of naphthalene is unusual, in that a third-order process is involved at only one of the two naphthyl positions. Any

reaction schemes must explain why the reaction having second-order kinetics operates exclusively at the 2-position, whereas the third-order reaction operates solely at the 1-position.

A satisfactory reaction scheme must also explain the following experimental observations: (*a*) the reaction at the 1-position is retarded by an excess of acetyl chloride, (*b*) there is a large primary kinetic hydrogen isotope effect at the 2-position, (*c*) there is a significant primary kinetic isotope effect at the 1-position when the concentration of free acetyl chloride is high; otherwise the effect is small, and (*d*) despite the variation in the magnitude of the kinetic isotope effects, the order of reaction at the 1-position remains 2 in the acetylating complex, and 1 in naphthalene.

In the literature on Friedel–Crafts acylations there are several reaction mechanisms which could give rise to third-order reaction kinetics, but in only two cases does the rate of reaction depend on the concentration of free acyl halide. One of these mechanisms, due to Corriu *et al.*,[11] cannot apply in the present case, because under certain limiting conditions that reaction would become independent of the concentration of naphthalene; details are given as a supplementary publication. [Sup. No. 56829 (9 pp.)*].

The reaction scheme. Jensen[6] and his co-worker Oziomek[5] have proposed a reaction scheme for the Friedel–Crafts benzoylation of naphthalene, which incorporates third-order kinetics. The scheme may be examined for the present acylation system. As acylation reagent the acetyl chloride/aluminium chloride addition complex (R) is preferred to the acetylium tetrachloroaluminate ion-pair, but an analogous scheme could be written for the latter. An initial, reversible, attack [eqn. (4)]

$$\underset{}{\mathrm{AcCl,AlCl_3}} + \mathrm{NH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(\sigma_1)}{\mathrm{NH,AcCl,AlCl_3}} \qquad (4)$$

by the reagent on naphthalene (NH), at either substituent position, leads to the formation of a σ-complex (σ_1), which may give the reaction product, the acetylnaphthalene/catalyst complex, in an irreversible decomposition step [eqn. (5)]. The

$$\mathrm{NH,AcCl,AlCl_3} \xrightarrow{k_2} \mathrm{AcN,AlCl_3} + \mathrm{HCl} \qquad (5)$$

sequence (4), (5) gives rise to 'normal' second-order kinetics. This is probably a sufficient description of the reaction at the 2-naphthyl position. However, the third-order kinetics for reaction at the 1-naphthyl position requires the inclusion of further reaction steps. Thus, the initially formed σ_1-complex may alternatively abstract a molecule of aluminium chloride from a second molecule of the acetylating complex with formation of another σ-complex (σ_2) and release of one molecule of acetyl chloride [eqn. (6)]. It is this reaction which

$$\mathrm{NH,AcCl,AlCl_3} + \mathrm{AcCl,AlCl_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(\sigma_2)}{\mathrm{NH,AcCl,2AlCl_3}} + \mathrm{AcCl} \qquad (6)$$

gives rise to the potential for third-order kinetics, and can account for acetyl chloride becoming a reactant in the reverse process (k_{-3}), as already suggested. A further decomposition stage [eqn. (7)] would lead to product, with release of uncomplexed aluminium chloride. The final step [eqn. (8)] reforms a molecule of acylating reagent.

$$\mathrm{NH,AcCl,2AlCl_3} \xrightarrow{k_4} \mathrm{AcN,AlCl_3} + \mathrm{AlCl_3} + \mathrm{HCl} \qquad (7)$$

$$\mathrm{AlCl_3} + \mathrm{AcCl} \xrightarrow{k_5} \mathrm{AcCl,AlCl_3} \qquad (8)$$

Kinetic analysis for the 1*-position.* The steady-state theorem, applied to the concentration of the second σ-complex (σ_2), leads to eqns. (9) and (10) (it is helpful to use abbreviations: n = [NH], r = [R] = [AcCl,AlCl$_3$], c = [AcCl$_f$], σ_1 = [σ_1] and σ_2 = [σ_2]). Similarly, the concentration of the σ_1-complex may be obtained *via* eqns. (11) and (12). The overall rate is then given by eqns. (13) and (14). This rate equation

$$\mathrm{d}\sigma_2/\mathrm{dt} = k_3\sigma_1 r - k_{-3}\sigma_2 c - k_4\sigma_2 = 0 \qquad (9)$$

$$\sigma_2 = \frac{k_3\sigma_1 r}{k_{-3}c + k_4} \qquad (10)$$

$$\mathrm{d}\sigma_1/\mathrm{dt} = k_1 rn - k_{-1}\sigma_1 - k_2\sigma_1 - k_3\sigma_1 r + k_{-3}\sigma_2 c = 0 \qquad (11)$$

$$\sigma_1 = \frac{k_1 rn}{k_{-1} + k_2 + k_3 r - k_{-3}c\sigma_2/\sigma_1} \qquad (12a)$$

$$= \frac{k_1 rn}{k_{-1} + k_2 + k_3 k_4 r/(k_{-3}c + k_4)} \qquad (12b)$$

$$\text{total rate at the 1-position} = k_2\sigma_1 + k_4\sigma_2 \qquad (13)$$

$$= \frac{k_1 k_2 rn}{k_{-1} + k_2 + k_3 k_4 r/(k_{-3}c + k_4)} + \frac{k_1 k_3 k_4 r^2 n}{(k_{-1} + k_2)(k_{-3}c + k_4) + k_3 k_4 r} \qquad (14)$$

differs from that derived for benzoylation of naphthalene by Oziomek[5] (as given in a Thesis, but not otherwise published), who curiously omitted the term k_3k_4r from the denominator of (14).

The rate equation (14) consists of two terms, the first being the second-order component, and the second the third-order component, of the overall reaction. Since the observed kinetics at the 1-naphthyl position are pure third-order, one may then discard the first term. This simplification is equivalent to the rate of the second step [eqn. (5)], *viz.* direct formation of the product from the σ_1-complex, being negligible compared to that of step (7), as expressed in eqn. (15). The simpler form of the rate expression is then eqn. (16).

$$k_2 \ll \frac{k_3 k_4 r}{k_{-3}c + k_4} \qquad (15)$$

$$\frac{\mathrm{d[1\text{-}AcN]}}{\mathrm{dt}} = \frac{k_1 k_3 k_4 r^2 n}{k_{-1}(k_{-3}c + k_4) + k_3 k_4 r} \qquad (16)$$

Eqn. (16) contains the concentration of acetylating reagent (r) not only in the numerator, but also as a term in the denominator. The effect of this latter term would be to reduce the apparent order of the reaction in this reagent. The observed pure third-order kinetics indicate that this term is, in fact, negligible; the consequence is that formation of the σ_1-complex is reversible, *i.e.* that the inequality in eqn. (17) applies. The final form of the rate equation is therefore eqn. (18).

* For details of the Supplementary Publication Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1991, Issue 1.

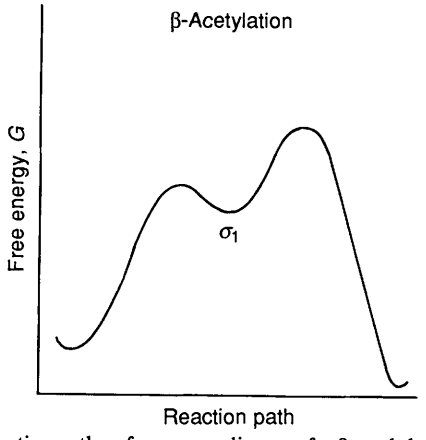


Fig. 3 Reaction path *vs.* free energy diagram, for β-naphthyl acetylation

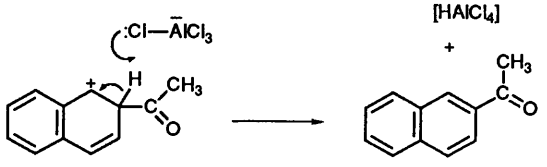


Fig. 4 Elimination of HCl from the σ-complex (ion-pair structure)

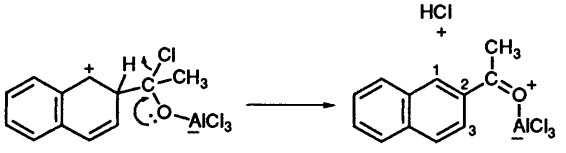


Fig. 5 Elimination of HCl from the σ-complex (oxonium structure)

$$k_{-1} \gg \frac{k_3k_4r}{k_{-3}c + k_4} \quad (17)$$

$$\frac{d[1\text{-AcN}]}{dt} = \frac{k_1k_3k_4r^2n}{k_{-1}(k_{-3}c + k_4)} \quad (18)$$

Eqn. (18) describes the predicted dependence of the rate of reaction at the 1-naphthyl position on the concentration of free acetyl chloride, (*c*). In order to examine this further, the ratio is taken of the third-order rate coefficient at the 1-position, defined by eqn. (18), to the second-order rate coefficient at the 2-position, k_β. This ratio was chosen, because in a given experimental run the ratio of these rate coefficients is obtainable to a higher accuracy than their absolute values. This ratio, $k_\alpha/k_\beta = p$, is then given by eqn. (19).

$$p = \frac{k_1k_3k_4}{k_\beta k_{-1}(k_{-3}c + k_4)} \quad (19)$$

When $c = 0$ the value of p is simply $k_1k_3/k_\beta k_{-1}$, and this is denoted by p_0. Setting $k_{-3}/k_4 = q$, one obtains the simplified relationship in eqn. (20a), or, inverting, eqn. (20b).

$$p = \frac{p_0}{1 + qc} \quad (20a)$$

$$\frac{1}{p} = \frac{1}{p_0} + \frac{qc}{p_0} \quad (20b)$$

A plot of *c vs.* $1/p$ for a series of experiments should then give a straight line with slope q and intercept $1/p_0$. Such a plot (data, at 0 °C, given in Table 2) is presented in Fig. 2: a good rectilinear relationship (correlation coefficient, $r = 0.9961$) obtains. This provides satisfactory confirmation for the above kinetic analysis. The derived value, $q = 11.9$ dm^3 mol^{-1} [98% confidence limits: ±1.0], is a measure of the extent of reversibility of the σ_2-complex, at zero excess acetyl chloride. From the intercept one obtains $p_0 = 137$ (±15) dm^3 mol^{-1}, the ratio k_α/k_β, in the absence of any free acetyl chloride. Using the mean experimental value of $k_\beta = 0.305$ dm^3 mol^{-1} s^{-1} (see above) one obtains $k_\alpha = 4.19$ (±0.48) dm^6 mol^{-1} s^{-1}. Since k_β is constant, a plot of *c vs.* $1/k_\alpha$ likewise should give a straight-line relationship, and does so ($r = 0.9873$), but use of the plot given in Fig. 2 is to be preferred for the reasons given.

Further Mechanistic Aspects.—To turn again to eqn. (18): in the presence of a large excess of acetyl chloride, the denominator can be simplified, as then $k_{-3}[\text{AcCl}] \gg k_4$. The equation becomes eqn. (21). This refers to a situation where formation of

$$\frac{d[1\text{-AcN}]}{dt} = \frac{k_1k_3k_4[\text{AcCl,AlCl}_3]^2[\text{NH}]}{k_{-1}k_{-3}[\text{AcCl}]} \quad (21)$$

the σ_2-complex [eqn. (6)] is at equilibrium and the rate of decomposition (k_4) of this complex is rate-limiting. This decomposition process must involve proton transfer, and therefore a kinetic hydrogen isotope effect is predicted, and is indeed observed.

In the absence of an excess of acetyl chloride the rate equation becomes eqn. (22). Under these circumstances the formation of

$$\frac{d[1\text{-AcN}]}{dt} = \frac{k_1k_3[\text{AcCl,AlCl}_3]^2[\text{NH}]}{k_{-1}} \quad (22)$$

the σ_2-complex becomes rate-limiting, and the rate coefficient k_4 does not appear in the rate equation. Therefore, no kinetic hydrogen isotope effect is to be expected, nor is observed.

The large kinetic hydrogen isotope effect observed for acetylation at the 2-naphthyl position indicates that proton transfer from that aryl position must be rate-limiting. This may be represented by the reaction path *vs.* free energy diagram, given in a general form in Fig. 3. For the 1-naphthyl position, the proton transfer must also be at least partly rate-limiting, provided an excess of acetyl chloride is present. The nature of the proton abstraction step is, therefore, an important aspect of the reaction mechanism.

It was argued above that, since the concentration of free acetyl chloride does not appear in the rate expression for 2-naphthyl acetylation, the proton transfer at this position must be essentially *intramolecular*.

Two possible forms of the σ_1-complex should be considered. The first is the ionic form arising from the interaction between acetylium tetrachloroaluminate ion pair and naphthalene; such a complex would almost certainly exist in the form of a tightly bound ion pair, having a common solvation shell (due to the low polarity of the solvent). The term *intramolecular* must then describe proton transfer between partners of the ion pair, in distinct contrast with proton abstraction by an external base molecule. Fig. 4 suggests the process most likely for the case of the 2-naphthyl reaction. The species $HAlCl_4$ involved, in fact, is one which has resisted all attempts at preparation; it clearly is not a stable molecule,[12] but is not inconceivable as a transient intermediate. It could then eliminate HCl, the $AlCl_3$ species complexing with the carbonyl oxygen of the ketone product. One can argue that hydrogen-abstraction by $AlCl_4^-$, which must be a very weak base, is unlikely. Therefore, the alternative form of the σ_1-complex, with an oxonium structure (Fig. 5) looks attractive. A concerted 1,2-elimination of HCl is here possible and results in the *direct* formation of the ketone/$AlCl_3$ product.

Such a concerted elimination requires a specific conformational alignment of H and Cl, as in Fig. 6: during the course

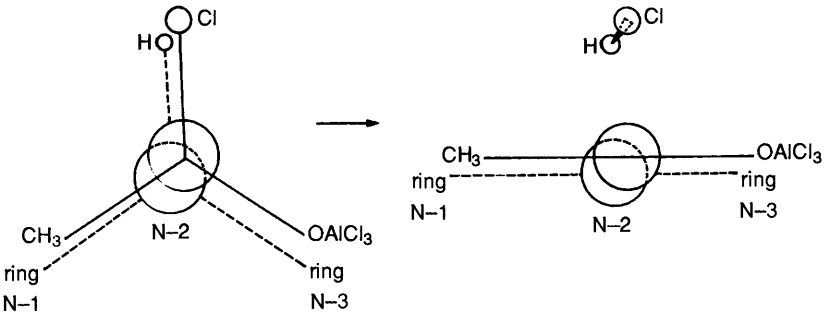


Fig. 6 Molecular conformation in the concerted elimination of HCl from β-naphthyl σ-complex

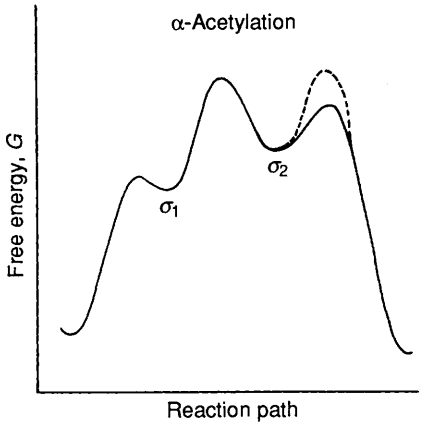


Fig. 7 Reaction path *vs.* free energy diagram, for α-naphthyl acetylation. (——) with no excess of AcCl; (– – – –) with excess AcCl.

of the reaction the acetyl function is drawn into the plane of the naphthalene rings, with consequent resonance stabilisation. This process looks entirely feasible for the reaction at the 2-naphthyl position. It explains why the simpler, second-order mechanism may operate in this case.

Any rotation of the acetyl group away from co-planarity, such as if occasioned by steric factors, would prevent the Cl atom from approaching close enough to the aryl-H atom. It is well established[13] that in 1-acetylnaphthalene the carbonyl function is normally rotated by at least 40° away from coplanarity with the naphthalene moiety through steric interaction with the *peri*-hydrogen atom, and this is likely to be accentuated by the presence of the aluminium chloride on the acyl oxygen. Such a σ_1-complex would not be stabilised by much conjugation energy, and consequently is of relatively high energy; hence the ease of reversibility of reaction (4).

In the case of reaction at the 1-naphthyl position, the above elimination of HCl being inhibited, a mechanism can proceed which allows the involvement of a second molecule of aluminium chloride. The acyl chlorine atom is removed with formation of a tetrachloroaluminate anion (the whole structure forming an ion pair), and the transfer of the proton can then take place by a sterically less demanding route. The existence of third-order kinetics for the α-reaction is therefore explicable in terms of reduced steric hindrance. The σ_2-complex for the α-reaction can be written with a near-orthogonal side chain (**IIa** or **b**); the latter (**IIb**) allows the negatively charged aluminium to swing down to a location (**IIIa** or **b**) quite close to the region of highest positive charge on the rings (due to optimal π-electron overlap in the phenylethene structure), this resulting in minimal separation of charges and maximal stability. The final proton transfer, as argued above, must be intramolecular. The sole candidate for a possible external base, AcCl, does not affect the rate of the β-reaction and actually tends to lower the rate of the α-reaction. The proton transfer therefore probably involves the $AlCl_4^-$ counterion. It would approach the naphthalene from the side opposite to the other negatively charged aluminium atom [as in **IV**], forming HCl and returning an electron-pair to the ring, to give the ketone/catalyst adduct, *i.e.* the ketonic product.

Fig. 7 presents the reaction path/free energy diagram for acetylation at the 1-naphthyl position. Using enthalpies as ordinate would be misleading; only with free energies is it possible to take account of entropy changes. The diagram shows that formation of the σ_1-complex is reversible. A second transition state leads to the σ_2-complex, and its decomposition finally leads to formation of the 1-acetylnaphthalene complex. The full line represents the path which occurs in the absence of free acetyl chloride: there is then no kinetic hydrogen isotope effect. The third transition state gradually increases in energy as the concentration of acetyl chloride increases; its formation becomes entropically less favourable (more negative $\Delta S^{\ddagger}$). The dotted line shows that a moderate kinetic isotope effect will be observed, and final loss of proton will then be partly rate-determining. The unusually low $\Delta S^{\ddagger}$ for the α-reaction (Table 3) supports this interpretation.

Conclusion

The rate data obtained in this work permit reaction conditions to be devised, for 1,2-dichloroethane solutions, which overwhelmingly favour the formation of either naphthyl isomer. It is best to avoid using free aluminium chloride, which would encourage resinification. In order to obtain predominant formation of the 1-isomer, one can use a high concentration of acetylating complex (*e.g.* 2 mol dm^{-3}) with naphthalene (1 mol dm^{-3}) and free acetyl chloride (0.1 mol dm^{-3}), the predicted proportion of 2-isomer being *ca.* 1%. The reaction will be 99% complete after 4 s at 0 °C. To obtain the 2-isomer as the predominant product, one may prefer using a complexing solvent, such as nitromethane.[14] If 1,2-dichloroethane is used as solvent, one would opt for a considerable excess of acetyl chloride and a low concentration of acylating complex. Employment of the Perrier addition sequence, with very slow addition of the complex to a solution of naphthalene,[15] could produce the necessary low concentrations. A product ratio $\alpha/\beta = 1/99$ would be hypothetically possible, but in practice a lower purity of 2-isomer is more likely.

It is regularly claimed, in text-books (*e.g.* ref. 16) and elsewhere, that the Friedel–Crafts acetylation of naphthalene is a reversible process, *viz.* that there is kinetic *vs.* thermodynamic control of products. Reversibility has been established[17] for acylations carried out in polyphosphoric acid solutions, but these are clearly non-Friedel–Crafts conditions. A reversible scheme was indeed considered as a possible explanation[18] of Friedel–Crafts acetylation data then available, but more recent work has shown[19] that reversibility is not significant for naphthalene itself, and only a marginal factor for certain substituted naphthalenes. The present paper, it is hoped, puts the matter into sharper focus, at least for one solvent.

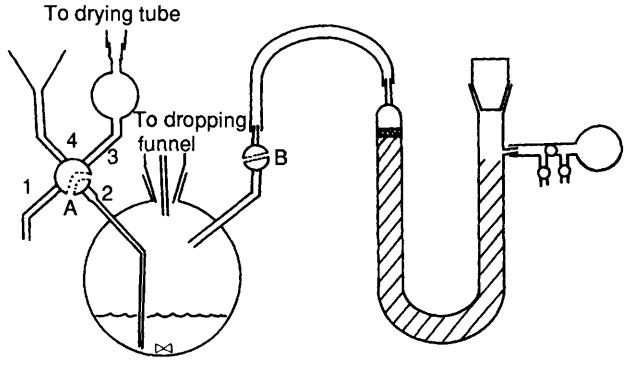


Fig. 8 The reaction vessel

Experimental

General Procedures.—Operations were performed, whenever possible, in a dry box (hereafter: DB) under nitrogen, or, where this was not feasible, the apparatus was assembled in a DB with outlets therefrom protected by P_2O_5 guard tubes. All glassware was thoroughly cleaned, then dried by heating in an oven, and allowed to cool in the DB. The precautions described below, which appear somewhat fanatical, were found by experience to be *necessary*. For example, just 40 ppm of water impurity in the solvent, for reactions carried out at typical reactant concentrations, could reduce the yield of ketones by up to 10%.

Sampling of the reaction mixture was performed in such a way that access of moist air was prevented whilst an aliquot was being taken. Since an internal standard was used (see below), the volume of the aliquot sample taken was not important, and a relatively simple and quick sampling procedure could then be developed.

Materials.—*1,2-Dichloroethane.* This compound (Aldrich, Gold Label) was washed twice each with conc. sulphuric acid, hydrochloric acid (3 mol dm^{-3}), aqueous sodium carbonate and water, then dried, initially by standing over anhydrous magnesium sulphate, then by boiling under reflux with an excess of phosphorus pentoxide for 2 h. This was followed immediately by fractional distillation using a 0.3 m Hempel column, the first and last 10% of solvent being discarded. A second such treatment with phosphorus pentoxide was then carried out, no agglomeration of the initial fine powder (indicative of the presence of moisture) taking place. This was followed by a final distillation. Both distillations were carried out in a large DB under a nitrogen atmosphere. The solvent was stored in a rigorously dried screw-cap bottle, and kept in a DB.

Aluminium chloride. BDH laboratory reagent grade aluminium chloride (Fe < 0.05%) was purified by sublimation[20] from fine aluminium powder, in a dry nitrogen atmosphere, under reduced pressure. The apparatus was assembled, and dismantled, in the DB. The sublimed catalyst, a fine white powder, was placed in a screw-cap sample tube, inside a screw-top jar (containing aluminium chloride granules), and kept in the DB. The catalyst was freshly prepared before each kinetic run.

Naphthalene. Naphthalene (Aldrich Gold Label), after recrystallisation from ethanol–water, and then from light petroleum (b.p. 40–60 °C), showed the presence, by careful GC analysis [carbowax 20M; or bentone/OV17 columns] of *ca.* 0.2% of impurity, believed to be benzo[*b*]thiophene.[21] A solution, prepared by dissolving aluminium chloride (3.3 g) and acetyl chloride (5 cm^3) in 1,2-dichloroethane (10 cm^3) was added dropwise to naphthalene (130 g) in the same solvent (200 cm^3) at 0 °C. After addition, the mixture was stirred at ambient temperature for 10 min, then quenched by addition of diethyl ether (50 cm^3) and water (50 cm^3). The organic layer was washed with dilute hydrochloric acid, and aqueous sodium carbonate, then dried over anhydrous sodium carbonate and concentrated. Isolation of naphthalene proceeded by either of two methods:

(*a*) after concentrating the solution to *ca.* 200 cm^3, it was passed through a column containing chromatographic silica (250 g), followed by washing with chloroform. The naphthalene eluted rapidly, whilst the ketone impurities were strongly retained. A final crystallisation (light petroleum, b.p. 60–80 °C) then gave pure naphthalene;

(*b*) After evaporation to dryness, the residue was subjected to steam-distillation, until no more naphthalene was carried over.

Naphthalene thus obtained was chromatographically pure, and gave no evidence of the presence of the more reactive benzo[*b*]thiophene, which would have been observed in kinetic experiments.

[$^2H_8$]*Naphthalene.* This material (Aldrich, '98 atom %') was used without further purification. A check of the isotopic purity was made by mass spectroscopy, a value of 97.8% being found: this corresponds to *ca.* 14% [$^2H_7$]naphthalene and traces of less deuteriated material. Since the protium in [$^2H_8$]naphthalene will have high reactivity, it was assumed that this protium has the same reactivity as a protium in normal naphthalene, and the appropriate small correction factor was applied. Details of the method are deposited as a supplementary publication.*

GC analysis did not reveal the presence of any chemical impurity, and no evidence of the presence of acetylbenzothiophenes was found after acetylation.

Acetyl chloride. Laboratory reagent grade (BDH) acetyl chloride was boiled under reflux for 2 h with phosphorus pentachloride, then distilled off, and finally fractionally distilled. It was stored in a dark screw-cap bottle in a DB.

Alkanes as internal standards. Octadecane (Fluka, 'purum'), nonadecane (Fluka, 'purum') and eicosane (Koch-Light, 'pure') were used as supplied.

Phosphorus pentoxide desiccant. The desiccant used in the drying tubes was supported phosphorus pentoxide with moisture indicator (BDH).

Kinetic Procedure.—The reaction vessel (Fig. 8) was a double-layer spherical flask, the outer compartment holding the constant temperature bath, the inner compartment housing the reaction medium. The constant temperature medium (*e.g.*, for 0 °C a crushed ice–water mixture) surrounded the inner flask almost completely. Three ground-glass joints allowed access to the reaction compartment. Both inner and outer compartments were supplied with a stirrer magnet.

For a typical kinetic run, a portion of aluminium chloride was transferred to a dry screw-cap sample tube, taken out of the DB, weighed and returned to the DB. The contents were then tipped into the reaction flask, which was stoppered immediately. The empty sample tube was reweighed, and the required quantities of the other materials were then calculated on the basis of the amount of the catalyst. The solvent was measured approximately (cylinder) into a weighed screw-cap bottle, which was taken from the DB, reweighed and returned. Naphthalene, and the internal standard, were similarly weighed into separate sample tubes. The required quantity of acetyl chloride was added to the solvent, which was then poured into the reaction flask. [It was observed that pure aluminium chloride caused a discolouration of the solvent, but not so in the presence of acetyl chloride.] The empty solvent bottle was weighed, and the volume of solvent calculated; a small correction was made for the trace of acetyl chloride also present. Finally the internal standard, the magnetic stirrer bar, and any additional components (if used) were added.

* See footnote on p. 1153.

For kinetic runs used in the determination of Arrhenius parameters, or the kinetic isotope effect, a stock solution of acetylating complex was used, prepared in a separate flask, and an appropriate quantity was then transferred to the reaction flask.

The weighed naphthalene was transferred to the dropping funnel (Fig. 8) with a measured amount of solvent, which rapidly dissolved it. The funnel was attached to the reaction flask by means of springs. Guard tubes containing the desiccant were attached to arms B and A3 by means of rubber tubing.

When completely assembled within the DB, the reaction apparatus was taken out and placed in an empty ice-bath above a magnetic stirrer motor. The flask was then stirred at room temperature until all the aluminium chloride had dissolved [the time needed varied from a few min to *ca.* 1 h, depending on the amount of acetyl chloride present]. A slurry of crushed ice–water was then added to the ice-bath, and to the cooling reservoir of the dropping funnel. Stirring was continued for *ca.* 1 h to achieve thermal equilibrium. During this time the tap on arm B was kept open, and the pipette filler was disconnected.

For Arrhenius experiments the ice–water mixture was replaced by an appropriate solution or mixture: for runs >0 °C water was used; for −10 °C an ice–salt–water mixture and for −23 °C an ice–calcium chloride–water mixture (cooled by solid carbon dioxide) were found suitable.

The reaction was started by opening the tap on the dropping funnel.

Sampling. Sampling for aliquots could be carried out at minimum intervals of 10 s. The procedure required two operators, one to work the pipette filler and taps, the other to place the correct (pre-labelled) collection vessel, or waste container, under the delivery arm.

The procedure (sampling sequence) was as follows: (1) tap B was opened; (2) the reaction vessel was slightly pressurised using the pipette filler, and simultaneously tap A was opened between arms 1 and 2 to deliver a sample; (3) tap A was turned off anticlockwise; (4) the reaction vessel was depressurised *via* the pipette filler; with this valve still open, tap A was opened between arms 2 and 3, thereby allowing the reaction mixture being retained in arm 2 to return to the main part of the reaction vessel; (5) the sample receiver was removed, and replaced by a waste container; (6) tap A was turned a further half-turn anticlockwise to connect arms 4 and 1; clean solvent was then run through the two arms, to wash out residual reaction mixture from arm 1; (7) if there was going to be a significant time interval before the next sampling, then tap B was closed; (8) the next sample receiver was placed under the delivery arm A1.

Quenching. The conventional quenching medium for Friedel–Crafts reactions, using a mixture of conc. hydrochloric acid and crushed ice, was not used. In the present work the medium was changed to diethyl ether containing a few drops of dilute hydrochloric acid. Because the reaction mixtures were very dilute, they did not require any cooling, nor any conc. hydrochloric acid to moderate the reaction and to keep all the components in solution. Instead, the overriding factor was the need for rapid quenching, to prevent further reaction. Since diethyl ether is miscible with 1,2-dichloroethane and complexes strongly with aluminium chloride, quenching is virtually instantaneous. With the conventional acid method, the green colour of the ketone/catalyst complex persists for several seconds, as water only slowly diffuses into the dichloromethane being used. Another advantage of the new technique is that on work-up nearly colourless products are obtained, whereas the traditional method gives yellow or brown products.

Work-up of samples. Two work-up procedures were investigated.

(1) Samples obtained as above (with water added) were extracted with diethyl ether (3 × 10 cm^3), the extracts were washed with a portion of water, which was back-extracted with more diethyl ether. The combined extracts were then dried ($MgSO_4$).

(2) Anhydrous sodium carbonate was added directly to the quenched reaction sample, in order to remove both water and hydrochloric acid directly.

In order to compare the two methods, a kinetic run was performed in which the two methods were applied to alternate samples. In addition, four samples were taken after 2 h (effectively complete reaction) with two samples being worked-up by each method. The results from *all* the samples fell on a single smooth curve, and there was no difference between any samples taken at 2 h. A similar analysis of four 2 h samples from two further runs confirmed this result. Therefore, method (2) was adopted as standard procedure, because of a considerable saving of time. The above samples were filtered to remove the desiccant, and nearly all the solvent was removed on a steam-bath. The flasks were then left open, at room temperature, for 1–3 h, until residual solvent had evaporated. Prior to GC analysis enough toluene was added to the samples to dissolve them completely.

GC Analysis.—The most reliable conditions of quantitative separation, which could be achieved in the necessary short time (5 min), used nonadecane as internal standard and a 0.5 m column containing 1.25% Bentone 34 and 3.75% OV17, with N_2 as carrier gas, at *ca.* 180 °C. Calibration, using weighed amounts of 1- and 2-acetylnaphthalenes, showed that the response factors of the isomers were the same, within experimental error (±1%). Mass response measurements were carried out with the internal standards, and were applied as appropriate.

Calculation of Rate Coefficients.—A priori one must consider four rate coefficients, *viz.* second-order and third-order rate coefficients at each naphthyl position. However, the results presented above (in particular Table 1) clearly demonstrate that the third-order reaction at the 2-naphthyl position is negligibly small. The analysis can be further simplified, by considering that the second-order reaction at the 1-position can also be neglected, since rate coefficients thus obtained are consistent both within and between runs. If there had been a significant second-order contribution to reaction at the 1-position, then the calculated third-order rate coefficients should decrease with increasing extent of reaction.

A more rigorous check was obtained by careful analysis of the early stages of the acylation reaction, as described as a supplementary publication.* This analysis indicated that the second-order rate coefficient at the 1-position is <5% of the corresponding rate coefficient at the 2-position. The method described below can therefore be used with confidence.

Under the foregoing assumptions the kinetic equations are (23) and (24), where a denotes [1-AcN], b denotes [2-AcN],

$$da/dt = k_\alpha n r^2 \quad (23)$$

$$db/dt = k_\beta n r \quad (24)$$

n denotes [naphthalene], r denotes [$AcCl,AlCl_3$]. These equations are linked *via* the concentrations of the reagents. They cannot, therefore, be integrated independently. Introducing $x = a + b$, and adding eqns. (23) and (24), one obtains eqn. (25) where subscript zero denotes a concentration at the start of the reaction.

* See footnote on p. 1153.

Table 6 Mass spectroscopic results (peaks heights) for competitive acylation [Experiment (*n*) (Table 5)][a,b]

	$C_{10}H_9^+$			$C_{10}H_9CO^+$			$C_{10}H_9COCH_3^+$			
m/z	127	133	134	155	161	162	170	176	177	170/(176 + 177)
1-AcN[c]										
1	3.86	0.40	1.01	4.69	0.95	1.23	2.53	0.51	0.64	2.200
2	6.01	0.57	1.60	7.18	1.50	1.85	4.05	0.79	1.05	2.201
3	4.24	0.43	1.08	5.04	0.98	1.34	1.79	0.54	0.74	2.184
Mean										2.195
s.d.										0.0095
2-AcN[c]										
1	5.21	0.23	0.96	6.44	0.24	1.23	3.62	0.16	0.69	4.176
2	3.59	0.14	0.58	4.31	0.18	0.83	2.38	0.10	0.47	4.258
3	6.37	0.25	1.17	7.81	0.28	1.47	4.28	0.22	0.83	4.076
Mean										4.170
s.d.										0.091

[a] All values are corrected for the ^{13}C component of the preceding peak. [b] Reactants: [naphthalene] = 0.114 mol dm^{-3}, [[$^2H_8$]naphthalene] = 0.113 mol dm^{-3}, [AcCl,$AlCl_3$] = 0.004 09 mol dm^{-3} and [$AcCl_f$] = 0.0942 mol dm^{-3}. [c] 1, 2 and 3 refer to repeat determinations.

$$dx/dt = k_\beta(n_0 - x)(r_0 - x) + k_\alpha(n_0 - x)(r_0 - x)^2 \quad (25a)$$

$$= k_\alpha(n_0 - x)(r_0 - x)(r_0 + k_\beta/k_\alpha - x) \quad (25b)$$

If $r_0 + k_\beta/k_\alpha$ in eqn. (25b) is replaced by s_0 one obtains eqn. (26), which is mathematically equivalent to the equation for a

$$dx/dt = k_\alpha(n_0 - x)(r_0 - x)(s_0 - x) \quad (26)$$

third-order reaction with three non-identical reagents.

This can be integrated to give eqn. (27).

$$k_\alpha t = \frac{1}{(r_0 - n_0)(n_0 - s_0)(s_0 - r_0)}\left[(s_0 - n_0)\ln\left(\frac{r_0}{r_0 - x}\right) + (r_0 - s_0)\ln\left(\frac{n_0}{n_0 - x}\right) + (n_0 - r_0)\ln\left(\frac{s_0}{s_0 - x}\right)\right] \quad (27)$$

Thus, k_α can be obtained if r_0, n_0 and s_0 are known. However, the latter quantity is a function of k_β/k_α, as noted above. It is therefore necessary to obtain this ratio, by dividing eqn. (24) by eqn. (25a), to give eqn. (28). On integration, this gives eqn. (29).

$$\frac{db}{dx} = \frac{k_\beta}{k_\beta + k_\alpha(r_0 - x)} \quad (28a)$$

$$= \frac{k_\beta/k_\alpha}{k_\beta/k_\alpha + (r_0 - x)} \quad (28b)$$

$$\frac{k_\beta/k_\alpha + r_0}{k_\beta/k_\alpha + (r_0 - x)} - \exp[-(k_\beta/k_\alpha)] = 0 \quad (29)$$

Eqn. (29) cannot be solved analytically, but a simple graphical method exists. The function described by the LHS of eqn. (29) is plotted against trial values of (k_β/k_α), and the correct value of the ratio is obtained at the point where the function is equal to zero. In practice this procedure was performed numerically using a computer.

In summary, the ratio k_β/k_α was obtained from eqn. (29). This was then used in eqn. (27) to obtain k_α. Finally k_β was obtained from these values.

Isotope Effect Experiments. [*Competitive method*].—A stock solution of 0.1 mol dm^{-3} acetylating complex was prepared in the usual way, and placed in a two-neck flask, having a septum and a P_2O_5 guard tube. For each reaction the appropriate amounts of naphthalene, [$^2H_8$]naphthalene (0.5 g), acetyl chloride, the internal standard and 1,2-dichloroethane were placed in similar flasks, cooled to 0 °C, and the reaction started by quickly injecting a calculated quantity of the acylating solution, with magnetic stirring. For each reaction the concentrations of substrates were > 10 times those of the acetylating complex. The reactions were quenched by pouring diethyl ether, containing a few drops of dilute HCl into the reaction mixtures. Sodium carbonate was then added, the mixtures filtered and evaporated, leaving a solid residue which was dissolved in a minimum quantity of chloroform. A small portion was set aside for standard GC analysis. The remainder was subjected to preparative TLC on silica, using 1 : 1 chloroform–light petroleum (b.p. 60–80 °C) [R_f = 0.9 (naphthalene) and 0.1 (acetylnaphthalenes); there was no fractionation of the two ketones]. Recovery of the separated products was achieved by warming the adsorbent with methanol, and washing with acetone. The ketone extracts were then evaporated. The isomers were separated by preparative GC, on a 1 m column of 5% Bentone 34 and 15% SE30 at 200 °C. This gave excellent separation with little tailing, and was ideal for the present case, of separating a small amount of 1-isomer from a large amount of the 2-isomer.

Mass spectral analysis was carried out on an AEI/Kratos MS 902 instrument with an electron impact source. Peak heights were used as a measure of the amount of an ion present. It was not possible to obtain spectra free from fragmentation, but since the spectra showed no significant isotope fractionation on fragmentation, it seemed reasonable to use the isotopic ratios for the parent ion as representative of the whole sample.

In one experiment (see Table 5) some isotopic scrambling was observed by the appearance of significant (M + 1) peaks for the undeuteriated species and enhanced (M − 1) peaks for the deuteriated species. This was observed in Experiment (*p*) to the extent of 10–15% of the molecules (1.5–2% of the hydrogen atoms); in this case the peak at *m/z* 171 ($C_{10}H_8DCOCH_3^+$) was added to the peak at *m/z* 170 ($C_{10}H_9COCH_3^+$) in the calculation of the isotope effect. Details of the mass spectral results of one Experiment [Table 5 (*n*)] are presented in Table 6.

Acknowledgements

We are particularly appreciative of the imagination and glass-blowing skills of Tony Williams.

References

1 L. Roux, *Ann. Chim. Phys.*, 1888, **12**, 189.
2 M. M. Anous, H. F. Bassilios, A. Y. Salem and M. M. Arab, *Z. Phys. Chem.*, 1970, **71**, 1. This work is critically assessed in ref. 3.
3 P. H. Gore, *Z. Phys. Chem., Neue Folge*, 1988, **159**, 123.
4 A. D. Andreou, R. V. Bulbulian, P. H. Gore, F. S. Kamounah, A. Y. Miri and D. N. Waters, *J. Chem. Soc., Perkin Trans. 2*, 1981, 376.
5 J. Oziomek, Ph.D. thesis, Univ. Microfilms, Ann Arbor, Michigan, 1968, order no. 69-3667; *Diss. Abstr. B.*, 1969, **29**, 3267.
6 F. R. Jensen, *J. Am. Chem. Soc.*, 1957, **79**, 1226; F. R. Jensen and G. Goldman, in *Friedel–Crafts and Related Reactions*, Interscience, 1964, Part III, p. 1024.
7 P. H. Gore, M. Jehangir and M. Yusuf, *Islamabad J. Sci.*, 1976, **3**, 16.
8 R. B. Girdler, P. G. Gore and J. A. Hoskins, *J. Chem. Soc. C*, 1966, 181.
9 F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, 1958, **80**, 3039; H. C. Brown, G. Marino and L. M. Stock, *J. Am. Chem. Soc.*, 1959, **81**, 3310.
10 G. A. Olah, S. J. Kuhn, S. H. Flood and B. A. Hardie, *J. Am. Chem. Soc.*, 1964, **86**, 2203; G. A. Olah and S. Kobayashi, *J. Am. Chem. Soc.*, 1971, **93**, 6964.
11 R. Corriu, M. Dore and R. Thomassin, *Tetrahedron Lett.*, 1968, 1759; *Tetrahedron*, 1971, **27**, 5601; 5819.
12 H. C. Brown and V. H. W. Pearsal, *J. Am. Chem. Soc.*, 1951, **73**, 4681.
13 W. B. Smith, D. C. Deavonport and A. M. Ihring, *J. Am. Chem. Soc.*, 1972, **94**, 1959; *cf.* P. H. Gore, J. A. Hoskins, C. K. Thadani, R. J. W. LeFèvre, L. Radom and G. L. D. Ritchie, *J. Chem. Soc. B*, 1969, 426.
14 G. Baddeley, *J. Chem. Soc.*, 1949, S99.
15 L. Friedman and R. J. Honour, *J. Am. Chem. Soc.*, 1969, **91**, 23.
16 D. L. Pavia, G. M. Lampman and G. S. Kriz, *Organic Laboratory Techniques*, 2nd edn., Instructors' Manual, Sanders College Publishing, 1988, 78.
17 I. Agranat, Y.-S. Shih and Y. Bantor, *J. Am. Chem. Soc.*, 1974, **96**, 1259; I. Agranat, personal communication, 1990.
18 P. H. Gore, *Chem. Rev.*, 1955, **55**, 242.
19 P. H. Gore and M. Yusuf, *J. Chem. Soc. C*, 1971, 2586; P. H. Gore, A. S. Siddiquei and S. Thorburn, *J. Chem. Soc., Perkin Trans. 1*, 1972, 781; P. H. Gore and A. S. Siddiquei, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1442; P. H. Gore, A. Y. Miri, J. Rinaudo and J.-M. Bonnier, *Bull. Soc. Chim. Fr.*, 1978, 107; P. H. Gore and M. Jehangir, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3007.
20 N. N. Gratzianskii, *Ukrain. Khim. Zhur.*, 1934, **9**, 432; P. C. Doolan, P. H. Gore and D. N. Waters, *J. Chem. Soc., Perkin Trans. 2*, 1974, 241.
21 D. Dowdy, P. H. Gore, J.-M. Bonnier and J. Rinaudo, *Chem. Ind. (London)*, 1985, 338.

Paper 1/00251A
Received 17*th January* 1991
Accepted 22*nd March* 1991