# The Friedel–Crafts Acetylation of Naphthalene. Evidence for Concurrent Second- and Third-order Reactions

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The Friedel–Crafts acetylation of naphthalene has been shown to give varying α : β isomer ratios as a function of concentration of the reactants. In consequence the ratio is strongly time- and temperature-dependent. Values of the α : β ratio (determined by an extrapolation procedure, for 1,2-dichloroethane solution) for the limit of zero reaction time, were plotted against reactant concentration, to give a straight line having a near-zero intercept. From this it is inferred that, whereas β-acetylation is essentially first-order with respect to the acylating reagent, α-acetylation is dominantly second-order in acylating reagent.

NUMEROUS reports have appeared on the remarkable variation of isomer proportions in the Friedel–Crafts acetylation of naphthalene. The factors known[1] to affect the α : β isomer ratio comprise the solvent, and the duration and temperature of the reaction.[2-6] Earlier work was handicapped by insecure methods of analysis,[4] the apparent inability of different groups of workers to reproduce the results obtained by other groups, and the proposal of fanciful theories.

In our own experience α : β isomer ratios are often reproducible only if reaction conditions are precisely duplicated. In nitromethane solution, for instance, with initial concentration of reagents (naphthalene and the acetyl chloride–aluminium chloride addition complex) = 1.28 mol dm$^{-3}$, the percentage of α-isomer remains constant with time, at least for times >0.5 h (Table 1). In 1,2-dichloroethane solution at two different initial concentrations of reactants, the percentage of α-isomer remains the same in each set, within experimental error (Table 2). However, since at the lower reactant concentration a lower percentage of α-isomer is obtained, then, as the reaction proceeds, the higher proportion of α-isomer might have been expected to give way to the lower, with a reduction of the overall percentage of α-isomer. The explanation must be that the reactions are virtually complete after 10 min; this is confirmed by the high yield of ketones obtainable under these conditions. The results indicate that there is a concentration-dependence of isomer proportions in the acetylation of naphthalene, and this has not been pointed out before.

TABLE 1

Acetylation of naphthalene in nitromethane solution at 20 °C at 1.28 mol dm$^{-3}$ of reactants

| Duration (h) | 0.5 | 1.0 | 5.0 | 20.0 | 30.0 | 90.0 | Mean (s.d.) |
|---|---|---|---|---|---|---|---|
| % α-Isomer | 24.0 | 24.7 | 25.3 | 25.5 | 24.0 | 23.7 | 24.5 (0.75) |

TABLE 2

Acetylation of naphthalene in 1,2-dichloroethane solution at 0 °C

(a) Concentration 1.28 mol dm$^{-3}$

| Duration (min) | 15 | 30 | 45 | 60 | 120 | Mean (s.d.) |
|---|---|---|---|---|---|---|
| % α-Isomer | 88.7 | 88.3 | 91.6 | 90.5 | 90.4 | 89.9 (1.4) |

(b) Concentration 0.200 mol dm$^{-3}$

| Duration (min) | 11 | 15 | 30 | 60 | 90 | 120 | Mean (s.d.) |
|---|---|---|---|---|---|---|---|
| % α-Isomer | 78.5 | 79.8 | 78.8 | 75.0 | 77.8 | 76.7 | 77.8 (1.7) |

A more clearcut example of this phenomenon was seen at low reactant concentrations, in chloroform solution (Table 3). Here a substantial increase of the percentage of α-isomer was observed to take place with increasing reaction time. The data suggest that the reaction is virtually over after *ca.* 15 min.

TABLE 3

Acetylation of naphthalene in chloroform solution at 20 °C, at 0.0625 mol dm$^{-3}$ of reactants

| *t*/min | 2 | 4 | 5 | 7 | 10 | 15 | 20 | 45 | 60 |
|---|---|---|---|---|---|---|---|---|---|
| % α-Isomer | 68.7 | 70.9 | 70.3 | 80.9 | 83.5 | 89.6 | 91.5 | 90.7 | 91.8 |

Concentration-dependence of the isomer proportions can be seen from more direct experiments conducted in chloroform (Table 4) and in nitromethane solutions (Table 5). In the latter reactions a *ca.* 10-fold increase in concentration produces an increase of α : β ratio from 0.176 to 0.522.

TABLE 4

Acetylation of naphthalene in chloroform solution for 30 min at 0 °C

| Concentration (mol dm$^{-3}$) | 0.100 | 0.200 | 0.500 | 0.800 | 1.28 | 1.80 |
|---|---|---|---|---|---|---|
| % α-Isomer | 37.8 | 49.8 | 63.3 | 71.3 | 77.5 | 78.6 |

TABLE 5

Acetylation of naphthalene in nitromethane solution for 30 min at 0 °C

| Concentration (mol dm$^{-3}$) | 0.190 | 0.500 | 0.800 | 1.00 | 1.28 | 1.80 |
|---|---|---|---|---|---|---|
| % α-Isomer | 15.0 | 15.8 | 22.1 | 20.5 | 27.2 | 34.3 |

Not in every case, however, is there an increase in percentage of α-isomer with time: with 1,1,2,2-tetrachloroethane the reverse holds true (Table 6). The

TABLE 6

Acetylation of naphthalene in 1,1,2,2-tetrachloroethane solution at 20 °C

(a) Concentration 0.300 mol dm$^{-3}$

| Duration (min) | 0.5 | 1.0 | 2.0 | 4.0 |
|---|---|---|---|---|
| % α-Isomer | 73.5 | 71.5 | 65.1 | 62.4 |

(b) Concentration 0.0300 mol dm$^{-3}$

| Duration (min) | 0.5 | 1.0 | 2.0 | 4.0 | 5.0 |
|---|---|---|---|---|---|
| % α-Isomer | 51.6 | 43.6 | 39.5 | 29.7 | 26.7 |

effect there is more pronounced at overall low concentrations.

The concentration effect is also apparent in a comparison of acetylations carried out over a range of temperatures (Tables 7 and 8). This is as expected, since at the higher temperatures more of the reaction will have taken place, and consequently in part at lower reactant concentrations. With an increase in reaction temperature the percentage of α-isomer decreases, monotonically in nitromethane solution (Table 7), but with a maximum at *ca.* 10 °C for 1,2-dichloroethane solution (Table 8).

TABLE 7

Acetylation of naphthalene in nitromethane solution for 30 min at 1.28 mol dm$^{-3}$ of reactants

| *T*/°C | −10 | 0 | 10 | 20 | 35 |
|---|---|---|---|---|---|
| % α-Isomer | 30.5 | 27.2 | 26.9 | 24.0 | 23.3 |

TABLE 8

Acetylation of naphthalene in 1,2-dichloroethane solution for 30 min at 0.200 mol dm$^{-3}$ of reactants

| *T*°C | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| % α-Isomer | 78.8 | 88.4 | 69.3 | 65.5 | 61.4 |

It appeared likely, in order to produce these widely varying proportions of α- and β-isomers, that the two competing substitution processes are kinetically dependent to a different degree on the concentration of the acylating reagent. In view of the very high proportions of the α-isomer obtainable at high reactant concentrations (99.5% α, see ref. 6), one could envisage that α-attack is second-order in acylating reagent, and β-attack is first-order in acylating reagent. This would put α-naphthyl acetylation in the same category as the third-order mechanisms which have been put forward, but not proven, for α-naphthyl benzoylation,[7] or acetylation at the 4-position of 1,2,3-trimethylbenzene (hemimellitene).[8]

We next considered the kinetics of two competing reactions, such as occur in naphthalene, to see if one could devise reaction conditions under which possible reaction schemes could be tested.

*Kinetic Analysis.*—If attack at the α- and β-positions follows the same kinetic order the α : β ratio will not vary with time. This does not correspond with the experimental evidence.

Suppose therefore, that α-attack is partly of third-order and partly of second-order [equation (1)], and β-attack is purely of second-order [equation (2)]. Then equation (3) holds

$$d\alpha/dt = k_1nr + k_3nr^2 \qquad (1)$$

$$d\beta/dt = k_2nr \qquad (2)$$

$$d\alpha/d\beta = (k_1 + k_3r)/k_2 = l + mr \qquad (3)$$

$d\alpha/dt$ represents the rate of formation of α-isomer

$d\beta/dt$ represents the rate of formation of β-isomer

$n = [N]$, where N = naphthalene,
$r = [R]$, where R = $CH_3COCl,AlCl_3$
$l = k_1/k_2$ and $m = k_3/k_2$.

Now $r = r_0 - \alpha - \beta$ where α and β are concentrations of α- and β-isomers formed, and $r_0 = [R]_0$. Therefore equation (4) holds. Multiplication by the integrating factor $e^{m\beta}$ permits this equation to be integrated.

$$d\alpha/d\beta + m\alpha = l + mr_0 - m\beta \qquad (4)$$

Using the values for $t = 0$, *i.e.* $\alpha_0 = \beta_0 = 0$, we obtain equation (5).

$$e^{m\beta} = \frac{l + mr_0 + 1}{l + m(r_0 - \alpha - \beta) + 1} \qquad (5)$$

To test the validity of this kinetic scheme, one may consider the limiting form of this equation applicable at small values of *t*. As $t \longrightarrow 0$, $\beta \longrightarrow 0$, and so the

$$e^{m\beta} \approx 1 + m\beta \qquad (6)$$

approximation (6) may be used at small values of time. Under these conditions, equation (7) follows. Thus as $t \longrightarrow 0$, equation (8) is obtained. Therefore, a plot of

$$\alpha/\beta = l + m(r_0 - \alpha - \beta) \qquad (7)$$

$$\alpha_0/\beta_0 = l + mr_0 \qquad (8)$$

$\alpha_0/\beta_0$ *versus* $r_0$ should be a straight line, with slope $m$ ($= k_3/k_2$), and intercept $l$ ($= k_1/k_2$). A special instance occurs if α-attack proceeds by a single, third-order mechanism. Then $k_1 = 0$, and equation (9) will apply, *i.e.* the plot will be a straight line of slope $m$, passing through the origin.

$$\alpha_0/\beta_0 = mr_0 \qquad (9)$$

It is possible, of course, that both α- and β-attack are kinetically complex, taking the forms (10) and (11). Then equation (12) holds where $s = k_1/k_2$, $t = k_3/k_2$, and $u = k_4/k_2$, leading to equation (13).

$$d\alpha/dt = k_1nr + k_3nr^2 \qquad (10)$$

$$d\beta/dt = k_2nr + k_4nr^2 \qquad (11)$$

$$d\alpha/d\beta = (k_1 + k_3r)/(k_2 + k_4r) = (s + tr)/(1 + ur) \qquad (12)$$

$$[1 + u\,(r_0 - \alpha - \beta)]\, d\alpha/d\beta = s + t\,(r_0 - \alpha - \beta) \qquad (13)$$

Equation (13) is a first-order differential equation which is non-linear. We have not found it necessary to pursue this equation, since, as we now show, equations (8) or (9) adequately represent the observed data.

α : β *Isomer Ratios under Limiting Conditions.*—In order to test the above possibilities [equations (8) and (9)], experiments were conducted with equal concentrations of reactants, *viz.* $n = r$ (see above), with reactions being carried out for short times (0.5—5.0 min), and α : β isomer ratios being then determined. For low concentrations (<0.06 mol dm$^{-3}$) and short reaction times the amount of ketones formed was very small, and one was working near the limit of the analytical procedure used. Values of α : β isomer ratios found on extrapolation to zero time are given in Table 9.

A plot of these α/β values *versus* initial concentrations of reactants is a satisfactory straight line (correlation coefficient 0.984), with a slope $m = 15.64 \pm 0.25$, and a

TABLE 9

$\alpha/\beta$ Isomer values, extrapolated to zero time, in the acetylation of naphthalene in 1,2-dichloroethane solution at 20 °C, as a function of initial concentration of reactants

| Concentration (mol dm$^{-3}$) | 0.040 | 0.050 | 0.070 | 0.090 | 0.100 | 0.110 |
|---|---|---|---|---|---|---|
| $\alpha/\beta$-Ratio | 0.727 | 0.677 | 1.145 | 1.336 | 1.559 | 1.761 |

very small intercept $l = 0.0210$. The best line which goes through the origin and the experimental points has correlation coefficient 0.998, and $m = 15.66 \pm 0.025$. Though the precision is not excellent, it is apparent that a simple relationship, *viz.* $\alpha_0/\beta_0 = 15.7r_0$ obtains satisfactorily here. Therefore one may conclude: (1) that, since $l \sim 0$, $k_1 \sim 0$; and, therefore, the reaction at the $\alpha$-position proceeds *via* a dominant third-order mechanism, with very little second-order component: and (2) that the ratio $k_3/k_2 = 15.7$ dm$^3$ mol$^{-1}$ in 1,2-dichloroethane solution at 20 °C. No information on the magnitude of these separate rate constants is available from this analysis. The scene is set for a detailed kinetic study of the acetylation of naphthalene.

## EXPERIMENTAL

The solvents were dried, and freshly distilled before use, by standard methods. Aluminium chloride was sublimed several times *in vacuo*. The reaction vessels were carefully dried by baking.

*Friedel–Crafts Acylations.*—The components, *viz.* naphthalene, acetyl chloride, and aluminium chloride, used in equimolar proportions, were brought together at the chosen temperature by the Perrier addition procedure, *i.e.* with final addition of the hydrocarbon to the pre-formed complex of acyl halide and catalyst. All the reactions were homogeneous throughout. For each experiment resublimed anhydrous aluminium chloride was carefully weighed out (*ca.* 0.8 g) and transferred to the reaction flask, in a dry box. A portion of acetyl chloride in the solvent, prepared as a stock solution, was added from a burette, followed by an appropriate volume of the solvent to make up the correct reagent concentration. The reaction flask was then thermostatted, the contents stirred magnetically, and the calculated quantity of naphthalene was added over 5 s. After the appropriate time interval the mixture was quickly poured onto a mixture of crushed ice and concentrated hydrochloric acid. The organic layer was separated, and to it was added a chloroform (or benzene) extract of the aqueous phase. The combined extract was then washed with 3N-HCl and water, dried ($Na_2SO_4$), and the solvent removed. The reaction product was then analysed by g.l.c. [(i) columns of 3% O.V.17 on 60—80 mesh Diatomite C, acid-washed and silanised with DMCS, at 200 °C, and $N_2$ as carrier gas; or (ii) WCOT column with a wall coating of O.V.17, 100 mesh, at 150 °C, and $N_2$ as carrier gas] at least twice. The replicate analyses were within 1%; the mass response of the f.i.d. was the same for $\alpha$- and $\beta$-isomers.

A typical result of the determination of $\alpha/\beta$-ratios as a function of time is given in Table 10.

TABLE 10

$\alpha/\beta$-Isomer ratios found experimentally, and as re-computed by the method of least-squares, for the acetylation of naphthalene in 1,2-dichloroethane solution at 20 °C, for initial concentration of reactants of 0.100 mol dm$^{-3}$

| $t$/min | $\alpha/\beta$-Ratio Found | $\alpha/\beta$-Ratio re-computed | Error (%) |
|---|---|---|---|
| 0.5 | 1.532 | 1.5224 | +0.63 |
| 0.5 | 1.512 | 1.5224 | −0.68 |
| 1.0 | 1.505 | 1.4859 | +1.29 |
| 1.0 | 1.491 | 1.4859 | +0.34 |
| 2.0 | 1.421 | 1.4130 | +0.57 |
| 2.0 | 1.380 | 1.4130 | −2.34 |
| 3.0 | 1.334 | 1.3401 | −0.46 |
| 3.0 | 1.337 | 1.3401 | −0.23 |
| 5.0 | 1.205 | 1.1943 | +0.90 |
| | | | Mean 0.83% |
| | $r$ 0.990 | | |

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