Kinetics of Protiodeacylation of 1-Benzoylnaphthalene and its Homologues in 89.8% Sulphuric Acid

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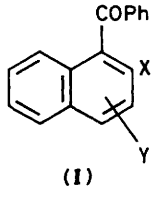
The kinetics of protiodebenzoylation in 89.8% (w/w) sulphuric acid have been measured for 1-benzoylnaphthalene and some of its methyl and dimethyl derivatives. Relative rate coefficients, calculated for 330 K, were (substituents in the naphthalene ring, relative rate): H, 1.00; 2-Me, 11.8; 4-Me, 96.2; 2,3-Me_2, 26.1; 2,4-Me_2, 67 000; 2,6-Me_2, 6 070; and 2,7-Me_2, 13 800.

The cleavage of benzoyl derivatives of aromatic systems, substituted at electronically activated but sterically crowded positions, when heated to 100 °C in syrupy phosphoric acid [1] or to 190 °C with concentrated hydrochloric or hydrobromic acid,[2] has been known for many years. Some kinetic studies of such protiodeacylations in moderately concentrated sulphuric acid have recently been reported, *viz.* the simple case of benzoylmesitylene,[3] and the more complex cases of dimesityl ketone[4] and 2,2',4,6,6'-pentamethylbenzophenone.[5] For ketones of the mesitylene series the benzoyl derivative reacts at *ca.* 1/250th the rate of the acetyl derivative, under the same conditions.[3] It has been stated[6] that acetophenones with two *ortho*-alkyl substituents react smoothly, and those with one alkyl substituent react with difficulty, though recent work[7] showed that 2-methylacetophenone undergoes protiodeacylation in 80.7 or 91.4% (w/w) sulphuric acid in the range 100—135 °C and the kinetics can be determined. Ketones with no *ortho*-methyl groups, it has been stated,[6] do not react.

In view of the higher reactivity of naphthalene, when compared with benzene, in electrophilic substitution reactions, suitably activated derivatives of 1-benzoylnaphthalene (**I**) were



(**I**)

a; X = Y = H
b; X = Me, Y = H
c; X = H, Y = 4-Me
d; X = Me, Y = 4-Me
e; X = Me, Y = 3-Me
f; X = Me, Y = 6-Me
g; X = Me, Y = 7-Me

investigated in the protiodeacylation reaction. 1-Benzoyl-2,4-dimethylnaphthalene (**Id**) was examined in 89.8% (w/w) sulphuric acid, and found to undergo smooth protiodeacylation in the range 8—35 °C (Table). The rate coefficient, extrapolated to 80 °C, is *ca.* 2.9×10^{-1} s^{-1}. This compares with the rate coefficient, measured[7] at 80 °C in 90.1% (w/w) sulphuric acid, for 1-acetyl-2,4-dimethylbenzene of 1.38×10^{-4} s^{-1}. It appears that ketone (**Id**) is remarkably reactive. Allowing for the rate factor acetyl/benzoyl *ca.* 250 (see above), it follows that introduction of the second ring causes a rate enhancement of *ca.* 5.3×10^5. Such activation is the result of the greater electron-density available at the 1-naphthyl position than at the corresponding phenyl position, combined with a steric enhancement of rate promoted by the hydrogen atom at the *peri* (8-) position of the neighbouring ring. The latter effect is confirmed by conformational studies[8] of 1-benzoyl-2-methylnaphthalene (**Ib**), albeit in non-polar solution, which suggests a dihedral angle of 75° between the C–CO–C and naphthalene planes. This non-planarity will reduce resonance stabilisation of the molecule, and promote the displacement of the benzoyl group by a proton.

Kinetic results were also obtained for other dimethyl-derivatives (**Ie—g**), and for 2- (**Ib**) and 4- (**Ic**) monomethyl-derivatives (Table). The rates for all these ketones are lower than for ketone (**Id**), yet even the monomethyl derivatives (**Ib, c**) could still be measured within an accessible temperature range, 80—105 °C. The parent compound (**Ia**) also smoothly underwent protiodebenzoylation. This ketone and the 4-methyl homologue (**Ic**) are the first examples of ketones not possessing activating *ortho*-methyl substituents which undergo the protiodeacylation reaction. It is especially notable that they are benzoyl derivatives, normally considered relatively unreactive. It may be recalled[9] that even in the absence of the *ortho*-methyl substituent, the carbonyl substituent is rotated away from stabilising coplanarity, a near-orthogonal dihedral angle (85°) being proposed (in CCl_4 solution) for the preferred conformation of ketone (**Ia**).

Rate data and activation parameters for the seven ketones are compared in the Table, at a mean experimental temperature (330 K). The activation enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) vary exceptionally widely, being both very high for the parent ketone (**Ia**) and very low for the 2,6-dimethyl compound (**If**),

Table. Rate coefficients and derived activation parameters, calculated at 330 K, for the protiodebenzoylation of 1-benzoylnaphthalene and its homologues, in 89.8% (w/w) sulphuric acid

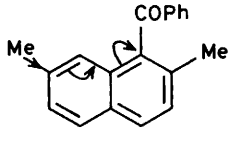
Compound	k_1/s^{-1} (computed)	k_{rel}	$\Delta H^{\ddagger}$[a]/kJ mol^{-1}	$\Delta S^{\ddagger}$[a]/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$[a]/kJ mol^{-1}
(**Ia**)	6.51×10^{-7}	1.00	155.8	+108	120.2
(**Ib**)	7.65×10^{-6}	11.8	130.3	+51.2	113.4
(**Ic**)	6.26×10^{-5}	96.2	84.7	−69.7	107.7
(**Ie**)	1.70×10^{-5}	26.1	100.0	−34.2	111.2
(**Id**)	4.36×10^{-2}	67 000	77.8	−36.1	89.7
(**If**)	3.95×10^{-3}	6 070	48.4	−145	96.3
(**Ig**)	8.99×10^{-3}	13 800	63.1	−93.6	94.0

[a] Mean errors: in $\Delta H^{\ddagger}$ ± 2.0%; in $\Delta S^{\ddagger}$ ± 9.8%; and in $\Delta G^{\ddagger}$ ± 2.9%.

and there is a good linear correlation between these parameters (overall $\rho = 0.987$). It has been pointed out[10] that many such apparently linear correlations are attributable to statistical artefact. The technique[10] of separating the 'statistical compensation effect' from any extrathermodynamic effects is based on a transformation from the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ plane to the $\Delta G^{\ddagger}/\Delta H^{\ddagger}$ plane, coupled with a linear transformation of $1/T$ with respect to the harmonic mean of the experimental temperatures. The present data were divided into two sets, according to the different experimental temperature ranges broadly covered. Using a computer program written for a BBC Master series computer,[11] good linear $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ correlations were found for both sets of ketones (ρ 0.9995 and 0.9997, respectively). The derived $\Delta G^{\ddagger}/\Delta H^{\ddagger}$ plots showed much poorer correlations (ρ 0.9265 and 0.8369, respectively), leading to the conclusion that no extrathermodynamic effects were present, and that there is no chemical causality for the highly correlated $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ plot.

The high $\Delta H^{\ddagger}$ values for ketones (**Ia**—**c**) exaggerate differences in rates computed for 330 K. At 365 K, within the experimental temperature range, the relative rates are (**Ia**):(**Ib**):(**Ic**):(**Ie**)::1.0:4.9:8.3:3.2. At first glance the greater reactivity of ketone (**Ic**) over ketone (**Ib**) would seem anomalous. It is clear that the *o*-methyl substituent in the latter does not exert added steric acceleration, since its presence evidently does not significantly alter the angle of rotation of the benzoyl function (see above). The electronic activation of C-1 would appear to be easier from the *para*-position, *i.e.* in ketone (**Ic**).

For the ketones with two methyl substituents, rate coefficients (at 330 K) increase in the sequence 2,3 ≪ 2,6 < 2,7 < 2,4. Since each of these ketones possesses a 2-methyl substituent, the effect on rate caused by substitution of an additional methyl group can be estimated. Thus, 3-, 4-, 6-, or 7-methyl, as second substituent, appears to cause an increase in rate coefficient at 330 K, by factors of *ca.* 2.2, 5 700, 510, and 1 200, respectively. It is clear that these substituent effects are not at all additive. If the 2- and 4-methyls in ketone (**Id**) were to affect the rate as they do in the monomethyl derivatives (**Ib** and **c**), a rate coefficient for ketone (**Id**) of 7.36×10^{-4} s^{-1} at 330 K would result; in fact the ketone (**Id**) reacts *ca.* 60 times as fast. The 6-methyl substituent in ketone (**If**), though rather remote from the site of reaction, yet produces a powerful effect. The even more pronounced effect of the substituent in ketone (**Ig**) may be the consequence of a methyl substituent rather closer to the reaction site; in addition, there may be a direct resonance effect [as in (**II**)].



(II)

Experimental

I.r. spectra were recorded for samples as KBr discs. ^{1}H N.m.r. spectra were obtained at 60 MHz in deuteriochloroform solution, with tetramethylsilane as internal standard.

The following ketones were prepared by literature methods. 1-Benzoylnaphthalene had m.p. 75 °C (lit.,[12] 76 °C). 1-Benzoyl-2-methylnaphthalene (**Ib**)[13] had m.p. 74—74.5 °C (lit.,[13] 74 °C) (Found: C, 87.7; H, 5.6. Calc. for $C_{18}H_{14}O$: C, 87.8; H, 5.7%); $\nu_{max.}$ 1 649 cm^{-1} (C=O) (lit.,[13] 1 648 cm^{-1}); δ_H 2.32 (3 H, s, Me) and 7.0—8.0 (11 H, m, Ar). 1-Benzoyl-4-methylnaphthalene (**Ic**)[13] had m.p. 73—74 °C (lit.,[14] 74—75 °C); $\nu_{max.}$ 1 655 cm^{-1} (C=O) (lit.,[14] 1 654 cm^{-1}); δ_H 2.62 (3 H, s, Me) and 7.0—8.3 (11 H, m, Ar). 1-Benzoyl-2,3-dimethylnaphthalene (**Ie**)[15] had m.p. 124—124.5 °C (lit.,[15] 126 °C); $\nu_{max.}$ 1 659 cm^{-1} (C=O) (lit.,[15] 1 659 cm^{-1}); δ_H 2.32 (3 H, s, 3-Me), 2.59 (3 H, s, 2-Me), and 7.3—8.1 (10 H, m, Ar) [lit.,[16] (CCl_4) 2.17, 2.41, and 7.0—7.9]. 1-Benzoyl-2,6-dimethylnaphthalene (**If**)[17] had m.p. 83—84 °C (lit.,[17] 84 °C); $\nu_{max.}$ 1 664 cm^{-1} (C=O) [lit.,[18] ($CHCl_3$) 1 656 cm^{-1}]; δ_H 2.28 (3 H, s, 6-Me), 2.42 (3 H, s, 2-Me), and 7.0—7.9 (10 H, m, Ar) (lit.,[18] 2.39, 2.50, and 7.2—8.1). 1-Benzoyl-2,7-dimethylnaphthalene (**Ig**)[19] had m.p. 91—91.5 °C (lit.,[19] 92 °C); $\nu_{max.}$ 1 666 cm^{-1} (C=O) (lit.,[19] 1 660 cm^{-1}); δ_H 2.31 (3 H, s, 7-Me), 2.42 (3 H, s, 2-Me), and 6.9—7.8 (10 H, m, Ar) (lit.,[19] 2.27, 2.34, and 7.1—8.0).

1-*Benzoyl*-2,4-*dimethylnaphthalene* (**Id**).—(a) 2,4-*Dimethyl*-1-*formylnaphthalene*.[20] This aldehyde was obtained as yellow crystals, m.p. 86—86.5 °C (lit.,[20] 86—86.5 °C); $\nu_{max.}$ 1 666 cm^{-1} (C=O) (lit.,[20] 1 670 cm^{-1}); δ_H 2.79 (3 H, s, 4-Me), 2.86 (3 H, s, 2-Me), 7.0—8.3 (5 H, m, Ar), and 11.6 (H, s, CHO) (lit.,[20] 2.64, 2.82, 7.5—8.9, and 11.4).

(b) (2,4-*Dimethyl*-1-*naphthyl*)*phenylmethanol*. The aldehyde (2.0 g) in dry tetrahydrofuran (10 ml) was added to freshly prepared excess of phenylmagnesium bromide at 5 °C. The mixture was stirred for 2 h, then poured into ice–hydrochloric acid. The product was isolated by extraction with chloroform, washing the extract with 10% sodium hydroxide solution, water, drying ($MgSO_4$), and evaporation of the solvent.

(2,4-*Dimethyl*-1-*naphthyl*)*phenylmethanol* formed yellow crystals (from ethanol) (1.81 g, 63%), m.p. 96—96.5 °C (Found: C, 87.0; H, 6.6. $C_{19}H_{18}O$ requires C, 87.2; H, 6.5%); $\nu_{max.}$ 3 150 cm^{-1} (OH); δ_H 2.46 (3 H, s, 4-Me), 2.68 (3 H, s, 2-Me), 3.71 (H, s, CH), and 7.4—8.8 (10 H, m, Ar).

(c) 1-*Benzoyl*-2,4-*dimethylnaphthalene*. The alcohol (1.09 g) in acetone (22 ml) was treated with Jones' reagent (1.0 ml), prepared by dissolving chromium trioxide (2.72 g) in water (4.0 ml) and concentrated sulphuric acid (2.3 ml), making the solution up to 10 ml, and keeping the mixture for 20 min. The solvent was then evaporated, the residue added to water (50 ml), and the mixture extracted with chloroform. The extracts afforded the *benzoyl derivative* as yellow crystals (0.70 g, 70%), m.p. 89—90 °C (Found: C, 87.65; H, 6.2. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%); $\nu_{max.}$ 1 666 cm^{-1} (C=O); δ_H 2.29 (3 H, s, 4-Me), 2.72 (3 H, s, 2-Me), and 7.1—8.1 (10 H, m, Ar).

Kinetics.—The kinetic procedures used have been given in earlier papers.[4,21]

Rate coefficients (s^{-1}, with T/K in parentheses) obtained were as follows. For ketone (**Ia**) 10^4k 0.823 (360.2), 1.88 (365.8), 3.25 (369.8), 5.18 (373.1), 5.47 (373.5), 8.71* (377.0), and 13.13 (380.0). For ketone (**Ib**) 10^4k 1.76 (353.0), 2.73 (356.2), 6.08 (362.5), 8.31 (365.2), 9.08 (366.0), 14.89 (370.3), and 21.2 (373.5). For ketone (**Ic**) 10^3k 0.506 (353.2), 0.659 (356.2), 1.128 (363.2), 1.335 (365.0), 1.93 (370.0), 2.09 (370.5), 3.00 (376.0), and 3.35 (376.8). For ketone (**Ie**) 10^4k 1.270 (348.8), 1.885 (352.8), 3.41 (358.5), 5.07 (362.6), 8.48* (368.7), and 13.30 (373.4). For ketone (**Id**) 10^3k 0.285 (281.8), 0.325 (283.0), 0.631* (288.2), 1.029 (292.7), 1.121 (293.2), 2.06* (299.0), 3.73 (304.6), 4.11 (305.6), and 5.53* (308.2). For ketone (**If**) 10^3k 1.043 (308.2), 1.528 (313.8), 2.16 (319.8), 2.27 (320.4), 2.46 (322.0), 3.08 (325.4), 3.31 (327.0), 3.68 (328.7), 4.49 (332.4), and 4.64 (333.0). For ketone (**Ig**) 10^3k 1.224 (304.6), 1.631* (308.2), 2.49 (313.2), 3.95 (319.0), 5.21* (322.6), and 7.28* (327.2).

* Mean of duplicate runs (mean ±0.7%).

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