Nucleophilic Substitution at a Trigonal Carbon. Part 5.[1] Substituent Effects in the Reactions of Aromatic Acyl Bromides with Methanol in Acetonitrile

Dennis N. Kevill and (the late) Donald C. Knauss
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA

The kinetics of the methanolysis of benzoyl bromide and eight *para*- or *meta*-substituted derivatives in acetonitrile at 25.0 °C can be analysed in terms of the simultaneous operation of overall second- and third-order processes. In turn, each of these processes can be analysed in terms of the simultaneous operation of two reaction channels, which are proposed to involve a carbonyl addition–elimination mechanism (favoured for electron-withdrawing substituents) and a process (S_N2–S_N1) proceeding through a loose S_N2-type transition state. For the *p*-methoxybenzoyl bromide substrate, a third reaction channel is observed, but only for the overall second-order process (first-order in methanol), and this is tentatively described as involving electrophilic assistance by a methanol molecule to an ionization (S_N1) pathway.

It has been shown previously that *p*-nitrobenzoyl chloride[2] and a series of aliphatic acyl halides[1,3] react with methanol in acetonitrile with the following of a kinetic scheme which involves terms of both first- and second-order in methanol (second- and third-order overall). The term of second-order in methanol was proposed to involve general-base catalysis by one methanol molecule towards nucleophilic attack by a second. The term of first-order in methanol could involve attack without general-base catalysis, or, and considered more likely, it could involve general-base catalysis by a solvent molecule. Enormous accelerations upon adding chloride ion are consistent with general-base catalysis. Chloride-ion addition (also the leaving group) could not lead to nucleophilic catalysis. Virtually no effect was observed upon addition of moderate concentrations of phenol, which would function better than the second methanol molecule as an electrophilic catalyst.

With the aliphatic acyl chlorides, a loose transition state, with a concerted S_N2 attack at the rearside of the carbon–chlorine bond was postulated for the parent acetyl chloride,[3] with a tightening of the transition state or a change to an addition–elimination mechanism upon introducing electron-withdrawing chloro substituents.[1] A parallel explanation has been given[4] for the effect of electron-withdrawing *para*-substituents in the reactions of benzoyl chlorides in binary mixtures of methanol with acetonitrile, nitrobenzene, or nitromethane. In the low basicity range of the mixed solvents, it was proposed that, in the presence of electron-withdrawing substituents, the reaction proceeded by the rate-determining carbonyl addition (addition–elimination) alternative.

In addition to studies with relatively small concentrations of a hydroxylic reactant in an inert solvent, there have also been studies under solvolytic conditions. The early studies of both types of system have been reviewed.[5] A study of the ethanolysis of a series of aliphatic acyl chlorides[6] showed that substituent effects could not be satisfactorily correlated in terms of the two-term Taft equation, incorporating the usual polar and steric substituent constants. A combination of addition–elimination and concerted displacement pathways[7] was considered as most likely but the operation only of a concerted pathway of variable transition state structure could not be excluded.

During the last decade, there have been several reports concerning the mechanism of solvolysis of the parent and substituted benzoyl chlorides. The mechanistic detail that has evolved is remarkably similar to that developed for parallel reactions carried out under non-solvolytic conditions. Similar to the behaviour towards 1% water in acetonitrile,[8] benzoyl chlorides with 2,6-dimethyl substituents are solvolysed in aqueous acetone, ethanol, or methanol primarily by the S_N1 mechanism, but S_N2 characteristics can be observed in the less aqueous methanol–water mixtures.[9] The S_N1 behaviour was also observed in the solvolysis of *p*-methoxybenzoyl chloride.[9,10] Song and Jencks[11] proposed dissociative (S_N1) mechanisms for the hydrolysis of *p*-methoxybenzoyl and *p*-(dimethylamino)benzoyl fluorides. For the latter compound, common-ion inhibition by fluoride ion was observed and, again, a change to a less aqueous solvent (60% ethanol) led to incursion of nucleophilic assistance from the solvent.

In studies of *para*-substituted benzoyl chlorides, competing carbonyl addition and S_N2 processes were proposed initially.[12,13] Subsequent study,[14] including product selectivities in aqueous alcohols, suggested that the process competing with carbonyl addition is better described as S_N1–S_N2 (S_N2 with a loose transition state). With the strongly electron-withdrawing *p*-nitro group, only the carbonyl addition process was observed[11,14] and the solvent deuterium isotope effect for hydrolysis suggested general-base catalysis by one water molecule to attack by a second.[11] Indeed, consistent with the general-base catalysis observed under non-solvolytic conditions, it has been found that good precision in rate–product correlations results if the kinetic analyses of solvolyses in aqueous alcohols are in terms of overall third-order rate coefficients.[15]

The solvolyses of several benzoyl chlorides (but not the *p*-nitro derivative) in water and aqueous 2,2,2-trifluoroethanol appear to follow a dissociative (S_N1) channel.[11] Fluoride ion strongly accelerates the hydrolysis of benzoyl chloride, presumably by general-base catalysis; however, the claim that this is strong evidence for nucleophilic participation by solvent, despite a ρ^+ value of -3.0, overlooks the possibility that there could be a powerful acceleration to a pathway which makes only a minor contribution in the absence of fluoride ion. We previously gave[2] an explanation of exactly this type for the pronounced chloride-ion catalysis to the predominantly dissociative reaction of chloroacetyl chloride with *p*-methoxyphenol in acetonitrile.[16]

Concerted acyl transfers have been proposed for reactions of *p*-nitrophenyl acetate with phenoxide ions[17–20] and theoretical arguments in favour of a concerted mechanism for these systems have been presented.[21]

In the present study, we report concerning the methanolysis, in acetonitrile as the solvent, of benzoyl bromide and a series of

Table 1 Experimental second-order rate coefficients (k'_2) for the reactions of 0.0400 mol dm^{-3} aroyl bromides (XC_6H_4COBr) with methanol, in acetonitrile at 25.0 °C

	$k'_2/10^{-3}$ dm^3 mol^{-1} s^{-1} [a]			
[MeOH]	*p*-NO_2 [b]	*m*-NO_2	*m*-Br [c]	*p*-Cl
0.631		14.9 ± 0.4	6.9 ± 0.2	4.67 ± 0.14
0.485	16.3 ± 0.8	13.0 ± 0.5		4.14 ± 0.08
0.318	12.3 ± 0.4	10.0 ± 0.6	4.60 ± 0.07	3.27 ± 0.11
0.160	9.8 ± 0.5	6.7 ± 0.2	3.43 ± 0.07	2.39 ± 0.10
0.0803	7.6 ± 0.4	5.7 ± 0.5	2.91 ± 0.16	2.15 ± 0.16

	$k'_2/10^{-3}$ dm^3 mol^{-1} s^{-1} [a]				
[MeOH]	*m*-MeO	H	*m*-Me	*p*-Me	*p*-MeO [d]
0.631	4.25 ± 0.14	4.50 ± 0.11	4.02 ± 0.12	3.97 ± 0.36	11.0 ± 0.4
0.485	3.55 ± 0.17	3.98 ± 0.09	3.56 ± 0.06	3.53 ± 0.09	10.2 ± 0.4
0.318	3.00 ± 0.07	3.53 ± 0.12	3.02 ± 0.08	2.83 ± 0.17	9.8 ± 0.2
0.160	2.16 ± 0.09	2.69 ± 0.17	2.52 ± 0.12	2.54 ± 0.16	9.1 ± 0.1
0.0803	2.02 ± 0.13	2.37 ± 0.15	2.23 ± 0.11	2.20 ± 0.16	9.3 ± 0.5

[a] Average of all points from duplicated runs, with associated standard deviation. [b] Also, with [MeOH] = 0.244 mol dm^{-3}, a value of 11.2 (±0.3) × 10^{-3} dm^3 mol^{-1} s^{-1}. [c] With 0.0200 mol dm^{-3} *m*-bromobenzoyl bromide, the corresponding values for $k'_2/10^{-3}$ dm^3 mol^{-1} s^{-1} are, reading downwards, 7.7 ± 0.2, 5.0 ± 0.1, 3.3 ± 0.2 and 3.1 ± 0.2; the experimental work with *m*-bromobenzoyl bromide was carried out by Mr. Dennis A. Centofante. [d] The values are after correction for a specific rate of background solvolysis of 0.18 × 10^{-3} s^{-1}; reading downwards, the original experimental values for $k'_2/10^{-3}$ dm^3 mol^{-1} s^{-1} are 11.3, 10.6, 10.4, 10.2 and 11.5.

Table 2 Second and third-order rate coefficients[a] for the reactions of 0.0400 mol dm^{-3} aroyl bromides (XC_6H_4COBr) with methanol in acetonitrile at 25.0 °C

X	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	$k_3/10^{-3}$ dm^6 mol^{-2} s^{-1}	r [b]	(k_3/k_2)/dm^3 mol^{-1}
p-NO_2	6.1 ± 0.3	20.8 ± 1.1	0.996	3.4 ± 0.2
m-NO_2	4.3 ± 0.4	17.4 ± 0.8	0.997	4.0 ± 0.4
m-Br	2.32 ± 0.03	7.1 ± 0.1	0.999	3.1 ± 0.1
m-Br [c]	2.18 ± 0.11	8.6 ± 0.4	0.995	3.9 ± 0.3
p-Cl	1.72 ± 0.09	4.8 ± 0.2	0.997	2.8 ± 0.2
m-MeO	1.62 ± 0.10	4.1 ± 0.2	0.996	2.5 ± 0.2
H	2.12 ± 0.11	3.9 ± 0.3	0.993	1.83 ± 0.17
m-Me	1.99 ± 0.02	3.21 ± 0.03	0.999	1.61 ± 0.02
p-Me	1.95 ± 0.09	3.18 ± 0.20	0.994	1.63 ± 0.13
p-MeO	8.8 ± 0.2	(3.3 ± 0.5)[d]	0.966	(0.38 ± 0.06)[d]

[a] Calculated from $k'_2 = k_2 + k_3$ [MeOH], using the data of Table 1; with associated standard errors. [b] Correlation coefficient for the plot. [c] With 0.0200 mol dm^{-3} *m*-bromobenzoyl bromide. [d] Of relatively low reliability, owing to the need to correct for background solvolysis coupled with relatively small variations in the value of k'_2 with changes in [MeOH].

derivatives with *para*- and *meta*-substituents of both electron-supplying and electron-withdrawing character.

Results

Reaction with Methanol.—The methanolysis of 0.04 mol dm^{-3} acetonitrile solutions of the parent benzoyl bromide and derivatives with *para*-nitro, *meta*-nitro, *meta*-bromo, *para*-chloro, *meta*-methoxy, *meta*-methyl, *para*-methyl and *para*-methoxy substituents were studied, in terms of the rate of acid production, at 25.0 °C, with a 0.08–0.64 mol dm^{-3} range of methanol concentration.

Experimental second-order rate coefficients, calculated according to eqn. (1), are reported within Table 1. The

$$d[HBr]/dt = k'_2[ArCOBr][MeOH] \qquad (1)$$

background rate of acid production, in the absence of methanol, was in the range 0.8–3.6% of the overall rate of acid production in the presence of the lowest concentration of methanol for all substrates except *p*-methoxybenzoyl bromide. The background value for *p*-methoxybenzoyl bromide constituted 19% of the overall rate of acid production with 0.08 mol dm^{-3} methanol and correlations were applied, as indicated in Table 1.

The kinetics for each substrate can be very well represented (correlation coefficient > 0.993, except for *p*-methoxybenzoyl bromide) by eqn. (2), and values for the second-order (k_2) and

$$d[HBr]/dt = k_2[ArCOBr][MeOH] + k_3[ArCOBr][MeOH]^2 \qquad (2)$$

third-order (k_3) rate coefficients are reported in Table 2.

The experimental data for individual runs can be treated in terms of eqn. (1) because of an approximation to second-order kinetics at low methanol concentrations coupled with an insensitivity towards order in methanol when it is present in a large excess over the aroyl bromide.

Reaction with Methanol in the Presence of Phenol.—The effect of added phenol was studied in the presence of an electron-withdrawing *p*-chloro-substituent and in the presence of an electron-supplying *p*-methoxy-substituent within the benzoyl bromide. Inspection of Table 3 shows that added phenol (0.04–0.32 mol dm^{-3}) has essentially no effect upon the rate of reaction of 0.04 mol dm^{-3} *p*-chlorobenzoyl bromide with 0.16 mol dm^{-3} methanol.

The corresponding methanolysis of *p*-methoxybenzoyl bromide was perturbed by the addition of phenol. In Table 4 is reported the effect of phenol on both the background rate of solvolysis and the overall second-order rate coefficient for acid production in the presence of 0.16 mol dm^{-3} methanol. Combination of the two sets of values allows tabulation of second-order rate coefficients, calculated according to eqn. (1) and corrected for both background solvolysis and possible reaction with phenol.

Discussion

Overall Kinetic Picture.—The experimental second-order rate coefficient for methanolysis (Table 1) can be analysed, for the parent benzoyl bromide and for four *para*- and four *meta*-substituted derivatives, in terms of overall second- and third-order rate coefficients[1–3] (Table 2). The rates of background solvolysis in the absence of methanol were negligible relative to the rates with at least 0.08 mol dm^{-3} methanol present, except for the study with *p*-methoxybenzoyl bromide where corrections of as great as 20% with the lowest methanol concentration were required. The solvolysis of *p*-methoxybenzoyl bromide was also unusual in having a much lower k_3/k_2 ratio (0.38 dm^3 mol^{-1}) than the other solvolyses (> 1.6 dm^3 mol^{-1}).

The k_3/k_2 ratio (Table 2) was found to decrease from a value of about 4 dm^3 mol^{-1} for strongly electron-withdrawing substituents to about 1.6 dm^3 mol^{-1} for a *p*-Me substituent. The upper limit is comparable to the value of 8.1 dm^3 mol^{-1} for methanolysis at 25.0 °C of *p*-nitrobenzoyl chloride in acetonitrile[2] and a similar range of values was found under parallel conditions, at 0.0 °C, with substituted acetyl chlorides, with values ranging from about 6 dm^3 mol^{-1} with electron-withdrawing chlorine substituents to about 2.5 dm^3 mol^{-1} with electron-supplying alkyl substituents. The close similarity in the k_3/k_2 ratios suggests that similar reaction pathways are involved in these studies.

The Hammett plots[22] constructed for each of the second- and third-order rate coefficients, according to eqn. (3), are shown in Fig. 1. In eqn. (3), k is the rate coefficient in the presence of a

$$\log k = \rho\sigma + \log k_0 \qquad (3)$$

substituent with an electron-withdrawing or -donating ability denoted by the Hammett σ value,[23] ρ is the sensitivity of the magnitude of the rate coefficient to changes in sigma value, and k_0 is the rate coefficient in the absence of a substituent.

Table 3 Second-order rate coefficients (k'_2)[a] for the reaction of 0.0410 mol dm^{-3} *p*-chlorobenzoyl bromide with 0.159 mol dm^{-3} methanol in the presence of varying concentrations of phenol, in acetonitrile at 25.0 °C[b]

[PhOH]/mol dm^{-3}	$k'_2/10^{-3}$ dm^{-3} mol^{-1} s^{-1}
0.0000	2.39 ± 0.10
0.0400	2.38 ± 0.12
0.0800	2.38 ± 0.12
0.163	2.35 ± 0.17
0.320	2.34 ± 0.06

[a] d[HBr]/dt = k'_2 [p-ClC$_6$H$_4$COBr] [MeOH]; with associated standard deviation. [b] Background solvolysis, with or without 0.163 mol dm^{-3} phenol, was found to be negligible after 8 min (the time for about 15% reaction with 0.159 mol dm^{-3} methanol).

The Hammett plots are both curved, with the plot involving k_2 values showing a minimum in the region of $\sigma = +0.1$ and the k_3 plot showing a levelling off with approximately constant values in the region of σ values from 0.0 to -0.3. For the k_2 plot, but not for the k_3 plot, there is a very marked increase in the log k value in going from *p*-Me ($\sigma = -0.170$) to *p*-MeO ($\sigma = -0.268$). These types of curve have been proposed[24] to arise from one or more of three possibilities. The curvature can result from variable transition-state structure within a single reaction channel, from the operation of two (or more) reaction channels with appreciably different ρ values, or from a different blend of polar and resonance effects in the reaction under consideration relative to the standard reaction used to establish the scale of σ values.[25,26] The third possibility seems unlikely for our systems since we have chosen equal numbers of *meta*- and *para*-substituted derivatives, and only the *para*-substituted derivatives have appreciable resonance contributions. The *meta*-substituted derivatives would not be expected to show variations of this type since direct resonance is not possible and only a small relayed resonance effect can operate.[27] Despite these differences both *meta*- and *para*-substituted derivatives lie on the same plots.

While a successful analysis cannot be considered to rule out the possibility of a variable transition state within one reaction channel, it is instructive to see how well the curves of Fig. 1 can be analysed in terms of a combination of two reaction channels.[12–14] This is done, in the next two sections of the discussion, for both third-order and second-order rate coefficients.

Analysis of the Third-order Rate Coefficients.—The possibility that the curvature is due to two reaction channels has been analysed by considering, in terms of eqn. (3), the approximately linear region of the plot (Fig. 1) in the presence of the electron-withdrawing *p*-Cl, *m*-Br, *m*-NO$_2$ and *p*-NO$_2$ groups. Values are obtained for $\rho = 1.17$ and for $\log k_0 = -2.594$ (correlation coefficient of 0.9995). These values are assumed to apply to a pathway we will classify as (A), and the contribution can be calculated for all nine substrates, to give log k_3(A) and hence k_3(A) values. The difference between the experimental k_3 (k_3^{expt}) values and k_3(A) can then be assumed to arise from a second mechanism (B) and, for the *p*-MeO, *p*-Me, *m*-Me, H and *m*-MeO substituents, consideration of [$k_3^{\text{expt}} - k_3$(A)] values leads to, in terms of eqn. (3), a ρ value of -1.22 and log k_0 value

Table 4 Rate coefficients for acid production from 0.0400 mol dm^{-3} *p*-methoxybenzoyl bromide (with associated standard deviations) in the presence of varying concentrations of phenol, both with and without 0.159 mol dm^{-3} methanol, in acetonitrile at 25.0 °C

[PhOH]	$k/10^{-3}$ s^{-1} [a]	$k'_2/10^{-3}$ mol^{-1} dm^3 s^{-1} [b]	k'_2(corr)/10^{-3} dm^3 mol^{-1} s^{-1} [c]
0.0000	0.118 ± 0.011	10.19 ± 0.14[d]	9.06
0.0400	0.277 ± 0.021	11.59 ± 0.58	9.81
0.0800	0.372 ± 0.025	13.43 ± 0.20	11.13
0.160	0.401 ± 0.010	16.35 ± 0.36	13.84
0.320	0.657 ± 0.028	18.85 ± 1.05	14.72
0.520	0.839 ± 0.009	24.91 ± 0.61	19.62

[a] Specific rate of acid production in absence of methanol and in the presence of the indicated concentration of phenol. [b] Experimental second-order rate coefficient for reaction with 0.159 mol dm^{-3} methanol in the presence of the indicated concentration of phenol: d[HBr]/dt = k'_2 [MeOH] [p-MeOC$_6$H$_4$COBr]. [c] k'_2(corr) = k'_2 − k/0.159. [d] Value from Table 1; a specific rate of background solvolysis of 0.180 (±0.015) × 10^{-3} s^{-1} is associated with this value.

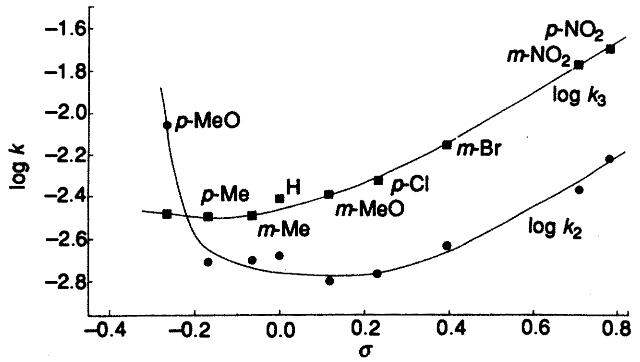

Fig. 1 Plot of the logarithms of the second-order (k_2/dm^3 mol^{-1} s^{-1}) and third-order (k_3/dm^6 mol^{-2} s^{-1}) rate coefficients for the methanolysis of substituted benzoyl bromides (XC_6H_4COBr) in acetonitrile at 25.0 °C against the Hammett sigma values for the substituents

of -3.002 (correlation coefficient of 0.919). The rather low correlation coefficient is due to an appreciable deviation for the unsubstituted (parent) compound and, if this is omitted from the series, values are obtained of -1.38 for ρ, -3.050 for $\log k_o$, and 0.9992 for the correlation coefficient. The k_3(B) contribution can then be calculated [eqn. (3)] for each of the nine substrates.

Addition of the estimated k_3(A) and k_3(B) values gives the k_3(A + B) values (Table 5) and these are found to be in excellent agreement with the k_3^{expt} values for all nine substrates. As mentioned above, while this gives conclusive evidence that the curvature of the plot *can* result from the simultaneous operation of two reaction channels, it cannot be considered to rule out the possibility that the curvature arises from variable transition-state structure within one reaction channel.

Analysis of the Second-order Rate Coefficients.—These have been analysed in a parallel manner to the analysis of the third-order rate coefficients. The approximately linear region for *m*-Br, *m*-NO_2, and *p*-NO_2 leads to a ρ value of 1.01 and a $\log k_o$ value of -3.035 (correlation coefficient of 0.980). These values were then used to give k_2(A) values for each of the nine substrates. Subtraction from experimental values gave [$k_2^{\text{expt}} - k_2$(A)] values which were similarly analysed, except the *p*-MeO substituent data point was omitted because the k_2^{expt} value was clearly too large to be included in an analysis of this type. Based on the parent compound and compounds with *p*-Me, *m*-Me and *m*-MeO substituents an analysis using eqn. (3) led to values for ρ of -1.69 and for $\log k_o$ of -3.076 (correlation coefficient of 0.857). The k_2(B) values can then be calculated, and k_2(A), k_2(B), k_2(A + B) and k_2^{expt} values are listed in Table 6. Except for the *p*-methoxybenzoyl bromide, there is reasonable agreement between the estimates for k_2(A + B) and the experimental values.

In consideration of third-order rate coefficients, the *p*-methoxybenzoyl bromide reaction gave good agreement between estimated and experimental values; this is not the case for the second-order rate coefficients. It appears that superimposed on the pathways A and B there is, for this substrate, an additional second-order pathway, accounting for 67% of the overall second-order reaction, which, unlike pathways A and B, is not accompanied by a corresponding third-order pathway. Since it is believed[1–3] that the overall third-order pathway results from general-base catalysis by one methanol molecule to attack by the second, it would appear that, in this additional pathway, the methanol is acting in a capacity which is not subject to general-base catalysis. Although we have no firm evidence in support, it is tempting to propose that the methanol now acts in an electrophilic capacity, leading to a $(p\text{-}MeOC_6H_4CO)^+(BrHOCH_3)^-$ ion pair by a pathway paralleling the one recently proposed for phenolysis of aliphatic acyl chlorides.[1,3] In support of this proposal is the finding by Gelles, Hughes and Ingold[28] that both phenol and ethanol accelerate the reaction of *tert*-butyl bromide in nitromethane, with ethanol being about one-fifth as effective as phenol. The *p*-methoxybenzoyl chloride has been shown to undergo S_N1 solvolyses and, indeed, it has been proposed as an improved standard substrate (relative to 1-adamantyl chloride) for establishing a scale of solvent ionizing power for use with structurally similar aroyl chlorides.[14]

Effect of Added Phenol.—The overall experimental second-order rate coefficients for reaction of *p*-chlorobenzoyl bromide with 0.159 mol dm^{-3} methanol at 25.0 °C are constituted to the extent of 69% by the second-order process (84% by pathway A) and 31% by the third-order process (92% by pathway A). Additions of phenol of up to 0.32 mol dm^{-3} have no effect upon the experimental second-order rate coefficient (Table 3). The lack of catalysis by added phenol is consistent with parallel additions to *p*-nitrobenzoyl chloride.[2] Similarly, additions of phenol to the methanolysis of acetyl chloride[3] and substituted acetyl chlorides[1] produced only very modest rate increases for additions of up to 0.32 mol dm^{-3}, and the overall kinetics could be approximately analysed in terms of the sum of the rates for the individual methanolyses and phenolyses.

With a *p*-methoxy substituent rather than a *p*-chloro substituent, phenol does accelerate both the background solvolysis and the experimental second-order rate coefficient for reaction with 0.159 mol dm^{-3} methanol. This is consistent with the proposed[14] tendency for *p*-methoxybenzoyl halides to react by the S_N1 mechanism. However, the effects are quite modest. Addition of 0.52 mol dm^{-3} phenol increases the specific rate of background solvolysis by a factor of seven, and it a little more than doubles the rate of reaction with 0.159 mol dm^{-3} methanol (Table 4). Only about 20% of the rate of reaction with 0.159 mol dm^{-3} methanol and 0.520 mol dm^{-3} phenol is due to reaction that would occur in the presence of phenol alone, and the doubling of the rate observed in the absence of phenol could result from either a medium effect of the relatively high concentration of phenol upon the methanolysis reaction or from a reaction pathway involving both phenol and methanol within the rate-determining step. A plot of the experimental second-order rate coefficients (after correction for rate of acid production due to presence of phenol), k'_2 (corr), against the phenol concentration is linear, with slope of 19.3 (± 1.9) × 10^{-3} dm^6 mol^{-2} s^{-1}, intercept of 9.4 (± 0.8) × 10^{-3} dm^3 mol^{-1} s^{-1} and correlation coefficient of 0.981.

Assignment of Mechanism to Reaction Channels (A) and (B).—Assuming that it is indeed correct to divide the overall second- and third-order rate coefficients into the two components (A) and (B), plus an apparent third reaction channel contributing towards the second-order rate coefficients for the *p*-methoxybenzoyl bromide methanolysis, one can speculate concerning the mechanisms. The third channel has already been discussed and, for these reactions at the S_N1 extreme of the S_N1–S_N2 spectrum, we have proposed electrophilic assistance by a methanol molecule to the ionization process. Accordingly, general-base catalysis is not relevant and this mechanism does not have an equivalent channel showing third-order kinetics.

It is helpful to survey the literature as an aid to rationalizing the pathways (A) and (B). The methanolysis of *p*-nitrobenzoyl chloride in acetonitrile was discussed[2] in terms of tetrahedral intermediates (carbonyl addition–elimination) and a concerted S_N2 process. A process involving tetrahedral intermediates was favoured. However, subsequent studies of the methanolyses in acetonitrile of acetyl chloride[3] and methyl-substituted derivatives[1] was rationalized in terms of a loose S_N2 transition

Table 5 Comparison of the sum of the predicted (best fit) third-order rate coefficients (for pathways A and B) and experimental values for the methanolysis of XC_6H_4COBr in acetonitrile at 25.0 °C

X	σ[a]	$k_3(A)/10^{-3}$ dm^6 mol^{-1} s^{-1} [b]	$k_3(B)/10^{-3}$ dm^6 mol^{-1} s^{-1} [c]	$k_3(A + B)/10^{-3}$ dm^6 mol^{-2} s^{-1}	k_3 expt/10^{-3} dm^6 mol^{-2} s^{-1} [d]
p-NO_2	+0.778	20.8	0.1	20.9	20.8
m-NO_2	+0.710	17.3	0.1	17.4	17.4
m-Br	+0.391	7.3	0.3	7.6	7.1
p-Cl	+0.227	4.7	0.4	5.1	4.8
m-MeO	+0.115	3.5	0.6	4.1	4.1
H	+0.000	2.6	0.9	3.5	3.9
m-Me	−0.069	2.1	1.1	3.2	3.2
p-Me	−0.170	1.6	1.5	3.1	3.2
p-MeO	−0.268	1.2	2.1	3.3	3.3

[a] From ref. 23. [b] Calculated using $\log k = 1.17\,\sigma - 2.594$. [c] Calculated using $\log k = -1.38\sigma - 3.050$. [d] From Table 2.

Table 6 Comparison of the sum of the predicted (best fit) second-order rate coefficients (for pathways A and B) and experimental values for the methanolysis of XC_6H_4COBr in acetonitrile at 25.0 °C.[a]

X	$k_2(A)/10^{-3}$ dm^3 mol^{-1} s^{-1} [b]	$k_2(B)/10^{-3}$ dm^3 mol^{-1} s^{-1} [c]	$k_2(A + B)/10^{-3}$ dm^3 mol^{-1} s^{-1}	k_2 expt/10^{-3} dm^3 mol^{-1} s^{-1} [d]
p-NO_2	5.6	0.04	5.6	6.1
m-NO_2	4.8	0.05	4.8	4.3
m-Br	2.3	0.18	2.5	2.3
p-Cl	1.6	0.35	1.9	1.7
m-MeO	1.2	0.54	1.7	1.6
H	0.92	0.84	1.8	2.1
m-Me	0.79	1.10	1.9	2.0
p-Me	0.62	1.6	2.3	2.0
p-MeO	0.50	2.4	2.9	8.8

[a] The σ values from ref. 23 and listed in Table 5. [b] Calculated using $\log k = 1.01\,\sigma - 3.035$. [c] Calculated using $\log k = -1.69\sigma - 3.076$. [d] From Table 2.

state, which tightened or changed to that for an addition–elimination process upon introduction of chloro-substituents.[1]

Our present observations are reminiscent of those observed for aroyl chlorides upon variation of solvent composition under solvolytic conditions. Evidence has been presented[12,13] that the solvolysis of the parent benzoyl chloride involves predominantly a carbonyl addition–elimination mechanism in ethanol-rich aqueous ethanol and predominantly a polar mechanism involving some S_N2 character in water-rich aqueous ethanol. In studies of substituent effects, the solvolysis of *p*-nitrobenzoyl chloride gave no evidence for mechanistic change and was assumed[14] to react by the carbonyl addition–elimination mechanism and, at the other extreme, *p*-methoxybenzoyl chloride was believed[14] to react by an essentially S_N1 process. Intermediate situations were successfully analysed in terms of two reaction channels, described as carbonyl addition–elimination and S_N2–S_N1 (S_N2 with a loose transition state) processes. Lee and coworkers[4] have also favoured a combination of these two reaction channels, rather than a concerted displacement with variable transition state, to describe the methanolysis of *para*-substituted benzoyl chlorides in binary mixtures.

We propose, in a parallel manner, that pathway (A) involves the carbonyl addition–elimination pathway, previously shown to be favoured for reactions of aroyl halides containing electron-withdrawing substituents[2,4,14] and pathway (B) involves a loose S_N2 transition state, such that positive charge tends to accumulate on the acyl carbon, and the transition state is stabilized by electron-donating substituents.[1,4,14]

Both of the pathways (A) and (B) are assisted by general-base catalysis, either by a second methanol molecule (overall third-order kinetics) or by an acetonitrile solvent molecule (overall second-order kinetics). The second-order kinetics pathway could represent nucleophilic attack by methanol without general-base catalysis but this is considered to be less probable because for methanolysis of *p*-nitrobenzoyl chloride in nitromethane, a poorer general base, no evidence for a second-order contribution was obtained and the overall kinetics could be accurately represented in terms of a third-order rate coefficient.[2]

Experimental

Materials.—Acetonitrile[29] and phenol[2] were purified as previously described. Methanol (Baker AR) was used without further purification. Benzoyl bromide (Eastman) and *m*-bromobenzoyl bromide (Eastman) were purified by vacuum distillation. The other substituted benzoyl bromides were prepared by the method of Adams and Ulich;[30,31] 0.09 mol of the sodium salt of the acid were refluxed in 50 cm^3 of benzene for 2 h with 0.12 mol of oxalyl bromide [eqn. (4)].

$$ArCO_2Na + (COBr)_2 \longrightarrow ArCOBr + CO + CO_2 + NaBr \quad (4)$$

After filtration, distillation of benzene and either vacuum distillation or recrystallization of the residue, the boiling or melting points were in good agreement with literature values.[30]

Kinetic Methods.—These were as previously described,[2] involving quenching in acetone at −78 °C and titration against a standardized solution of triethylamine in toluene, except that it was rare to see the usual red to blue colour change of the resorcinol blue (Lacmoid) indicator. Usually, the observed colour change was from red to green or yellow. The neutral blue form of the resorcinol blue must have reacted rapidly with unchanged aroyl bromide, under the conditions of the titration, to give yellow derivatives. A similar situation operated in parallel reactions of chloro-substituted acetyl chlorides.[1]

Acknowledgements

D. C. K. was supported by the National Science Foundation Undergraduate Research Participation Program.

References

1 Part 4, D. N. Kevill and C.-B. Kim, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1353.
2 D. N. Kevill and F. D. Foss, *J. Am. Chem. Soc.*, 1969, **91**, 5054.
3 D. N. Kevill and C.-B. Kim, *Bull. Soc. Chim. Fr.*, 1988, 383.
4 I. Lee, D. D. Sung, T. S. Uhm and Z. H. Ryu, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1697.
5 (*a*) A. Kivinen, in *The Chemistry of Acyl Halides*, ed. S. Patai, Interscience, New York, 1972, ch. 6; (*b*) R. J. E. Talbot, in *Comprehensive Chemical Kinetics*, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 10. pp. 226–227.
6 D. N. Kevill, P. H. Daum and R. Sapre, *J. Chem. Soc., Perkin Trans. 2*, 1975, 963.
7 M. Cocivera, Ph.D. Thesis, University of California, Los Angeles, 1963.
8 M. L. Bender and M. C. Chen, *J. Am. Chem. Soc.*, 1963, **85**, 30.
9 T. W. Bentley, H. C. Harris and I. S. Koo, *J. Chem. Soc., Perkin Trans. 2*, 1988, 783.
10 T. W. Bentley, I. S. Koo and S. J. Norman, *J. Org. Chem.*, 1991, **56**, 1604.
11 B. D. Song and W. P. Jencks, *J. Am. Chem. Soc.*, 1989, **111**, 8470.
12 T. W. Bentley, G. E. Carter and H. C. Harris, *J. Chem. Soc., Perkin Trans. 2*, 1985, 983.
13 T. W. Bentley and H. C. Harris, *J. Chem. Soc., Perkin Trans. 2*, 1986, 619.
14 T. W. Bentley and I. S. Koo, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1385.
15 T. W. Bentley and H. C. Harris, *J. Org. Chem.*, 1988, **53**, 724.
16 J. M. Briody and D. P. N. Satchell, *J. Chem. Soc.*, 1965, 168.
17 S. Ba-Saif, A. K. Luthra and A. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6362.
18 S. Ba-Saif, A. K. Luthra and A. Williams, *J. Am. Chem. Soc.*, 1989, **111**, 2647.
19 S. Ba-Saif, M. Colthurst, M. A. Waring and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1901.
20 A. Hengge, *J. Am. Chem. Soc.*, 1992, **114**, 6575.
21 J. P. Guthrie, *J. Am. Chem. Soc.*, 1991, **113**, 3941.
22 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1987, 3rd edn., pp. 143–159.
23 J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963, p. 173.
24 P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 3288.
25 Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1959, **32** (*a*) 965; (*b*) 971.
26 Y. Yukawa, Y. Tsuno and M. Sawada, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2274.
27 J. Shorter, *Correlation Analysis of Organic Reactivity*, Research Studies Press, Chichester, England, 1982, p. 31.
28 E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1954, 2918.
29 D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, 1969, **34**, 1985.
30 R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, 1920, **42**, 599.
31 O. Ito, T. Sakaguchi and M. Matsuda, *J. Chem. Soc.,, Faraday Trans. 1*, 1978, **74**, 1188.

Paper 2/06140F
Received 18*th November* 1992
Accepted 3*rd December* 1992