The Electronic Effect of the Phenylazo and t-Butylazo Groups

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Hammett σ_p^+-values for arylazo and t-butylazo groups have been determined by measurements of the kinetics of solvolysis of the appropriately substituted arylpropan-2-yl chlorides. They have been found to be considerably more positive than expected and differ significantly from earlier estimates based on the rates of electrophilic attack on azobenzene. An interpretation of the discrepancy has been advanced based on the differing orientations of the azo linkage with respect to the aromatic ring in the transition state. The introduction of methyl groups into positions *ortho* to the phenylazo and t-butylazo substituents causes a change in character from $-I$, $-R$ to $-I$, $+R$. This is true not only for the solvolysis reaction but also for benzoic acid ionisation.

The electronic effect of the phenylazo group has not been widely studied, but it is generally recognised as electron-withdrawing in most circumstances. Taft and co-workers [1] estimated σ_I values for the group of +0.19 in non-polar solvents and +0.25 in methanol, based on ^{19}F n.m.r. chemical shift studies of *meta*-substituted fluorobenzenes. A number of σ_m- and σ_p-values have been reported, and on the basis of these Exner has proposed values of +0.29 and +0.33 respectively, as the best estimates.[2] Comparison of these with the results of Taft's σ_I values show that for benzoic acid ionisation the phenylazo substituent is $-I$, $-R$ in character. For most $-R$ substituents σ_I is about 0.05—0.08 lower than σ_m, suggesting that in aqueous solution σ_I is probably *ca.* +0.22, a value in good agreement with those of Taft.

Several σ_p-values have been reported, ranging from +0.55 in Me_2SO to +0.69 in protic solvents.[3] The latter figure makes the group a relatively strong resonance-withdrawing agent, comparable in strength to an acetyl or nitro group, but substantially weaker than a nitroso group ($\sigma_p^- = +1.46$[4]) a substituent to which it is more closely related structurally.

In view of its strong $-R$ character it is therefore surprising to find evidence that, under suitable circumstances, it can ac as an overall electron-donor. In kinetic studies of electro philic substitution in azobenzene, σ_p^+ values as low as −0.4 ave been reported.[5] Perhaps the most striking feature of these studies, however, is the wide range of reported values (see Table 1).

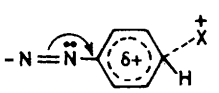
It is unlikely that the scatter is due to the involvement of different substitution mechanisms in each case. The most likely source of the variable reactivity of azobenzene towards electrophiles would seem to be the geometric relationship between the phenyl rings and the azo linkage. In the electrophilic substitution process, stabilisation of the transition state leading to the formation of the Wheland intermediate can be achieved by overlap of the ring π-system with either the lone pair of the adjacent azo nitrogen or the π-system of the azo linkage. However, since the two orbitals are orthogonal, one or the other must tend to be favoured. This explanation was advanced by us in an earlier paper[8] where we observed that bromination of azobenzene using acidified hydrobromous acid was much slower than anticipated.

It is unlikely that the situation is one where the electrophile chooses between two substrates, planar and non-planar azobenzene. A more reasonable interpretation is that initial attack occurs on the 'planar' form, which is believed to be the major form in solution,† and that, concerted with the formation of the σ-bond between the electrophile and substrate, rotation of the azo group occurs to bring the lone pair on the adjacent azo nitrogen into a position where it can be more effective in stabilising the system. The extent of this rotation could well depend on whether the transition state leading to the Wheland intermediate occurs early or late along the reaction co-ordinate.

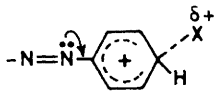
Table 1. Literature σ_p^+-values for the phenylazo group reaction

Reaction	σ_p^+
Rate of chlorination,[5] AcOCl, 97.9% AcOH–H_2O, 25 °C	−0.4
Rate of chlorination,[5] Cl_2, AcOH, 25 °C	−0.04[a]
Rate of chlorination,[6] Cl_2, 80% AcOH–H_2O, 25 °C	−0.1[a]
Rate of nitration,[7] HNO_3 in Ac_2O, 0 °C	−0.187
Rate of bromination,[8] HOBr/H^+ in 75% dioxane–H_2O, 25 °C	+0.09

[a] Based on estimated *ortho*:*para* ratio of 30:70 and $\rho \approx -10$.



Early transition state



Late transition state

Such an interpretation would lead to the expectation that reactions involving the most reactive electrophiles, which should have the most 'reactant-like' transition states, should yield the least negative σ_p^+-values.

There is some evidence that of the electrophiles cited in Table 1, the one present in the bromination reaction is the most reactive towards benzene, and this is also the one associated with the most positive σ_p^+-value. However, the high negative value for the chlorine acetate reaction would seem anomalous, if this interpretation is correct, as chlorine acetate reacts faster than chlorine under the same conditions.[5]

We decided that further investigation of the system was warranted. Rather than vary the nature of the attacking electrophile we decided to examine the effect of changes in the substrate structure. Because of the potential effect of such changes on isomer distribution, and resulting difficulties in determining partial rate factors, it was decided to look instead at their effect on the rate of solvolysis of the appropriately substituted cumyl chlorides, the system chosen by H. C. Brown in his pioneering work on σ_p^+-constants.[10] In our case this system had the added advantage of yielding σ_p^+-constants for which there was no possibility of ambiguity with regard to the mechanism of the reaction.

† There is some question as to the degree of planarity of azobenzene in solution. Some evidence suggests that the phenyl groups are twisted slightly out of the plane of the azo linkage.[9]

Two types of change in the substrate structure were investigated: (i) the effect of substitution in the arylazo ring of 2-[4-(arylazo)phenyl]propan-2-yl chloride and its replacement by t-butyl was studied. Any effect on reactivity was expected to be relatively small but it was hoped that it might provide some information as to the efficiency of transmission of electronic effects through the azo linkage, which in turn might indicate the configuration. (ii) The steric effect of introducing two methyl groups in positions on either side of the azo group was examined. These substituents, it was felt, should impose some constraint on the geometrical relationship between the aromatic ring and azo group and thereby modify its resonance effect significantly. It was also considered that, if the steric interaction between the azo linkage and the two methyl groups was sufficiently great, then this might also be reflected in changes in the σ_p^+-value, perhaps to the extent of making the group a $-I$, $+R$ one for benzoic acid ionisation. For this reason it was decided to determine the pK_as of the corresponding 3,5-dimethylbenzoic acids, compounds that could be readily prepared from intermediates in the cumyl chloride syntheses.

Results and Discussion

The pK_a and solvolysis results are summarised in Tables 2 and 3 respectively. Hammett substituent constants, calculated for all azo groups using ρ-values derived from the other substituents for which σ-values are well known, have been listed in Table 4.

Electronic Effects.—Preliminary consideration of the results for the unhindered arylazo and t-butylazo derivatives shows a normal pattern of behaviour, with the t-butylazo group values closely paralleling those for phenylazo. The difference between σ_m for the two suggests that for t-butylazo the σ_I is lower, probably by around 0.04 units. This is in the direction, and of the order of magnitude, that one would expect. Differences between their σ_p and σ_p^0 values are somewhat greater and show that phenylazo has the stronger $-R$ effect of the two.

Their σ_p^+-values differ only marginally, and by an amount that appears to reflect mainly the difference between their σ_Is. However, this difference is of much less significance than their actual values, which, together with those for the other arylazo groups, are very much more positive than expected. That for phenylazo is nearly 0.1 units higher than the highest previously reported (positive bromination of azobenzene) and very much higher than any of the others. Furthermore, on the basis of their estimated σ_I-values, the phenylazo and t-butylazo groups have very small σ_R^+-values, certainly less than -0.05.

On the basis of our previous explanation for the variability of σ_p^+ in electrophilic substitutions, the relatively high positive σ_p^+s require that for the solvolysis reaction the azo linkage and the phenylene ring be coplanar, or nearly so, in the transition state, because the low σ_R^+s can only be explained by assuming that σ_p^+ is a composite value reflecting contributions from σ_I, σ_R^+, and σ_R^0, with the latter two opposing one another. For the σ_R^0 contribution to be positive, at least some degree of coplanarity is essential. It will be noted that the σ_p^0-values for phenylazo and t-butylazo are both more positive than the corresponding σ_p ones. The differences are not great, and, given the lower reliability of σ-values derived from phenylacetic acid ionisations, could be considered to lie within normal error limits. However, if real, they provide some support for the simultaneous operation of $+R$ and $-R$ effects in systems of this type, although alternative explanations such as variations in the $-R$ effect of the group cannot be ruled out.

The effect of substituents in the ring of the phenylazo group is superficially what we might expect, in that electron-donating groups tend to lower σ_p^+ and withdrawing groups raise it. For two of these (4-fluorophenylazo and 3-bromophenylazo) σ_p^+-values of $+0.09$ and $+0.20$ respectively were obtained in our earlier investigation of positive bromination of azobenzene.[8] When one considers that in that system σ_p^+ for phenylazo was $+0.09$ the results in our present study do not appear too far out of line. Quantitative examination of the data reveals two features of significance. First, the transmission of inductive effects through the azo linkage is more than twice as efficient in the electrophilic substitution as in the solvolysis reaction, and second, the *p*-MeO derivative reacts about twice as fast as would be predicted from consideration of the rates of the other substrates.

The first may be related to the distance of the substituent from the reaction site, as the solvolysis result is similar to that observed for reactions of phenols and anilines.[11] The second is more puzzling as it implies that the Hammett equation has broken down. Normally this is evidence for a change in mechanism, which here would most likely involve a significant change in the structure of the transition state. Unfortunately, the abnormal rate enhancement in our case is most logically associated with a lesser degree of coplanarity of the system, whereas a strong $+R$ group such as OMe should, in fact, increase it. At present we can offer no satisfactory explanation for this result.

Steric Effects.—Schaefer and Miraglia[12] measured the pK_as of 4-substituted 3,5-dimethylbenzoic acids and concluded that for some substituents significant steric inhibition of resonance can exist, although this was never so great as to eliminate it altogether. These workers calculated that the acetamido group, a substituent having a steric requirement closest to that of our azo group, was twisted at an angle of 49° relative to the phenyl group. Recently, Zerner and co-workers[9] examined the effect of *ortho*-substitution on the electronic spectra of azobenzenes. They concluded that in both 2,6-dimethylazobenzene and 2,2′,6,6′-tetramethylazobenzene the dimethylphenyl rings are twisted out of the plane of the azo group by an angle of about 40°. This they attributed to repulsion between the methyls and the lone pair on the distant nitrogen.

Our results are in accord with those reported by these two groups. They are summarised in the two columns on the right in Table 4 as 'hindered' σ_p- and σ_p^+-values, derived from the data for the derivatives with flanking methyl groups by correcting them for the electronic contribution of the latter. In all cases there has been a substantial decrease in the magnitude of the σ-value, consistent with an enhanced ability of the azo system to act as a resonance donor. For benzoic acid ionisation, the effect is to change the azo group from $(-I, -R)$ to $(-I, +R)$ in character. For the solvolysis reaction, a system in which it is already $(-I, +R)$, the $+R$ effect is increased leading to a substantial lowering of σ_p^+. For phenylazo this change brings it below that obtained for positive bromination of azobenzene, but still leaves it significantly above that reported for other substitutions (Table 1). Undoubtedly, this decrease in σ_p^+ is related to a combination of increased participation by the lone pair in the stabilisation of the transition state together with a decreased contribution from the $-R$ effect due to loss of coplanarity. It would be unwise, however, to try and relate the reactivity of the molecule to the actual transition state geometry by comparison of data for azo compounds with and without the methyl groups.

The introduction of methyl groups into flanking positions on the far ring has relatively little overall effect, presumably because the electronic and steric effects of the methyls offset one another. There is no sign in the tetramethyl derivative of effects attributable to steric interactions between the methyls of the two rings.

The most surprising result in the hindered system, however, is the result for the t-butylazo derivative. For benzoic acid

ionisation the result is in line with that for phenylazo, but for the solvolysis the derivative is very much more reactive than anticipated. The result for the 2′,6′-dimethylphenylazo compounds show that a steric effect is unlikely to explain the discrepancy. In contrast, an enhanced electronic effect also appears unlikely as this would also be expected to affect σ_p to a significant extent. No such behaviour is observed. Like the *p*-OMe result, this is a feature of our investigation for which we can at present offer no satisfactory explanation.

On the whole, however, we feel that our results are in reasonable accord with our proposed explanation for the variations for σ_p^+ reported in the literature. One unexpected bonus of our investigation is that it raises questions about the overall composition of a substituent effect. A number of workers, the most notable being Taft[13] and Swain,[14] have produced multiparameter extensions to the Hammett equation based on the 'total' resolution of substituent effects into inductive and resonance contributions. Our results would suggest that the resonance term, at least in the case of σ_R^+ and σ_R^-, carries a distinct σ_R^0 component. Both Taft and Swain assume that ρ_R is the same for all of the existing resonance contributions in the system. Such an assumption may not be justified in all cases, particularly in ones such as ours, where σ_R^0 and σ_R^+ have different signs.

Experimental

Preparation of Compounds.—The benzoic acids, phenylacetic acids, and 2-propyl chlorides used as standards were either commercial samples or prepared by literature methods. All were known compounds.

Phenylazobenzoic Acids.—In the preparation of these compounds, the azo linkage was, in all but one example, formed by a condensation reaction between a nitroso compound and a primary amine. Equimolar quantities of the two reagents were heated in acetic acid for a few hours on a steam-bath. The crude product was subjected to chromatography, carried out by a Harrison Research Inc. Model 7924 Chromatotron using rotors coated with a 2 mm layer of silica gel (Merck PF_{254} type 60) and with ether–light petroleum (b.p. 50—70 °C) mixtures as eluant. Separation was considerably assisted by the fact that the desired products were coloured. Brief details of the methods used are given below. Only the 3- and 4-phenylazobenzoic acids have been previously reported.[15,16]

3-*Phenylazobenzoic acid.* Condensation of nitrosobenzene with methyl 3-aminobenzoate gave methyl 3-phenylazobenzoate (44%). Saponification of the ester gave the acid, m.p. 165—166 °C (lit.,[15] 166—167 °C).

4-*Phenylazobenzoic acid.* The above method with ethyl 4-aminobenzoate gave 4-phenylazobenzoic acid, m.p. 233—235 °C (lit.,[16] 204 °C) in similar yield.

2-[4-(*Phenylazo*)*phenyl*]*acetic acid.* Condensation of nitrosobenzene with ethyl 4-aminophenylacetate followed by saponification gave the title compound, m.p. 196—197 °C (Found: C, 69.9; H, 5.2; N, 11.6. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%).

3,5-*Dimethyl*-4-*phenylazobenzoic acid.* Condensation of ethyl 4-amino-3,5-dimethylbenzoate with nitrosobenzene gave the azo ester, which on saponification gave 3,5-*dimethyl*-4-*phenylazobenzoic acid*, m.p. 195—197 °C (Found: C, 71.0; H, 5.8; N, 11.1. $C_{15}H_{14}N_2O_2$ requires C, 70.9; H, 5.6; N, 11.0%).

4-(2′,6′-*Dimethylphenylazo*)*benzoic acid.* Condensation of ethyl 4-nitrosobenzoate with 2,6-dimethylaniline gave the azo ester in very low yield. Saponification gave 4-(2′,6′-*dimethylphenylazo*)*benzoic acid* as red needles, m.p. 171—172 °C (Found: C, 70.9; H, 5.6; N, 10.8. $C_{15}H_{14}N_2O_2$ requires C, 70.9; H, 5.6; N, 11.0%).

3,5-*Dimethyl*-4-(2′,6′-*dimethylphenylazo*)*benzoic acid.* 2,6-Dimethylnitrosobenzene would not react with aromatic amines to give azo compounds. The above product was prepared *via* its ethyl ester by the oxidative cross-coupling of 2,6-dimethylaniline and ethyl 4-amino-3,5-dimethylbenzoate.[17] Ethyl 4-amino-3,5-dimethylbenzoate (5.2 g), 2,6-dimethylaniline (13.1 g), and silver(I) carbonate supported on Celite (2 mol equiv.) were refluxed for 13 h in toluene (400 ml). The mixture was filtered and the toluene evaporated off to give a dark red residue, which was subject to chromatography on a silica gel column with 1:1 benzene–light petroleum (b.p. 50—70 °C). Initial elution gave 2,2′,6,6′-tetramethylazobenzene (3.4 g), whereas subsequent elution with benzene gave a dark red solid. Further purification of this on the Chromatotron gave pure ethyl 3,5-dimethyl-4-(2′,6′-dimethylphenylazo)benzoate (1.2 g), m.p. 60—62 °C. Saponification using KOH–ethanol followed by crystallisation from methanol gave purple crystals of the required acid, m.p. 212—213 °C (Found: C, 72.7; H, 6.6; N, 10.0. $C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.4; N, 9.9%).

t-Butylazobenzoic Acids.—The preparations of these differed from those of the arylazobenzoic acids only in that the condensation step was carried out by the method of Barton.[18] In this approach the appropriate aromatic nitrosoester is stirred in benzene solution overnight with t-butylamine and t-butyl hypochlorite. The coupling product in this instance was the t-butyl-*NNO*-azoxy derivative which was subsequently converted into the corresponding azo compound by reduction with zinc dust followed by oxidation with yellow mercury(II) oxide. Saponification yielded the desired acid. All compounds were new. Analytical data are given below.

3-*t-Butylazobenzoic acid*, m.p. 130—131 °C (Found: C, 63.9; H, 7.00; N, 13.7. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.9; N, 13.6%).

4-*t-Butylazobenzoic acid*, m.p. 183—184 °C (Found: C, 64.3; H, 6.8; N, 13.7. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.9; N, 13.6%).

3,5-*Dimethyl*-4-*t-butylazobenzoic acid*, m.p. 207—209 °C (Found: C, 66.5; H, 8.1; N, 11.7. $C_{13}H_{18}N_2O_2$ requires C, 66.6; H, 7.7; N, 12.0%).

Arylazoaryl- and t-Butylazoaryl-propanols and 2-Propyl Chlorides.—The substituted propanols were prepared by the inverse addition of an excess of ethereal methylmagnesium iodide to solutions of the appropriate ethoxy carbonyl derivatives in either diethyl ether or tetrahydrofuran. The crude products were purified by chromatography using the Chromatotron. In about half the cases the ester derivatives were already available, having been prepared as intermediates for the carboxylic acid syntheses. The rest were prepared either by the condensation of ethyl 4-nitrosobenzoate with the appropriate aromatic amine (4-OMe, 3-Br) or ethyl 4-aminobenzoate with the appropriate nitroso derivative (4-Me, 4-F, 4-Br).

2-[4-(*Phenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 91 °C (Found: C, 75.2; H, 7.0; N, 11.7. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%).

2-[3,5-*Dimethyl*-4-(*phenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 58—60 °C (Found: C, 76.1; H, 7.5; N, 10.2. $C_{17}H_{20}N_2O$ requires C, 76.1; H, 7.5; N, 10.4%).

2-[3,5-*Dimethyl*-4-(2′,6′-*dimethylphenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 63—64 °C (Found: C, 77.1; H, 8.5; N, 9.5. $C_{19}H_{24}N_2O$ requires C, 77.0; H, 8.2; N, 9.5%).

2-[4-(2′,6′-*Dimethylphenylazo*)*phenyl*]*propan*-2-*ol* was isolated as a red oil (Found: $M^{+\bullet}$, 258.158. $C_{17}H_{20}N_2O$ requires *M*, 268.158. The product appeared to be pure by ^{13}C n.m.r. spectrometry but failed to give a satisfactory combustion analysis.

2-[4-(4′-*Methylphenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 94—95 °C (Found: C, 75.5; H, 7.2; N, 11.0. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%).

2-[4-(4′-*Methoxyphenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 104—105 °C (Found: $M^{+\cdot}$, 270.137. $C_{16}H_{18}N_2O_2$ requires $M^{+\cdot}$ 270.137). The product appeared pure by ^{13}C n.m.r. spectrometry but failed to give a satisfactory combustion analysis.

2-[4-(4′-*Fluorophenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 103—104 °C (Found: C, 69.6; H, 5.9; F, 7.3; N, 10.7. $C_{15}H_{15}FN_2O$ requires C, 69.8; H, 5.9; F, 2.4; N, 10.9%).

2-[4-(4′-*Bromophenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 113—114 °C (Found: C, 56.4; H, 4.7; Br, 25.5; N, 8.5. $C_{15}H_{15}BrN_2O$ requires C, 56.4; H, 4.7; Br, 25.0; N, 8.8%).

2-[4-(3′-*Bromophenylazo*)*phenyl*]*propan*-2-*ol*, m.p. 69—70 °C (Found: C, 56.7; H, 4.9; Br, 24.9; N, 8.8. $C_{15}H_{15}BrN_2O$ requires C, 56.4; H, 4.7; Br, 25.0; N, 8.8%).

2-[4-(*t-Butylazo*)*phenyl*]*propan*-2-*ol*, m.p. 69 °C (Found: C, 70.6; H, 9.5; N, 12.6. $C_{13}H_{20}N_2O$ requires C, 70.9; H, 9.2; N, 12.7%).

2-[3,5-*Dimethyl*-4-(*t-butylazo*)*phenyl*]*propan*-2-*ol*, m.p. 58 °C (Found: C, 72.5; H, 9.8; N, 11.2. $C_{15}H_{24}N_2O$ requires C, 72.5; H, 9.7; N, 11.3%).

2-*Propyl chlorides*. The 2-propyl chlorides were all prepared by reaction of the corresponding propanol with an excess of thionyl chloride. To a stirred solution of the propanol (100 mg) in anhydrous dichloromethane (5 ml) thionyl chloride (0.3 ml) was added and the solution was stirred for 30 min. The solvent was evaporated off under reduced pressure and any excess of thionyl chloride removed by pumping under high vacuum. The purities of the carbinyl chlorides obtained were checked by ^1H n.m.r. but their identity was not checked by microanalysis.

pH Measurements.—Potentiometric data were recorded on a Radiometer PHM 64 instrument using a Beckman 39004 glass electrode and a Beckman 39071 calomel electrode. The electrode system was standardised against aqueous NBS borax and phthalate buffers (pHs 9.183 and 4.0880 respectively).[19] The system was calibrated as a $[H^+]$ probe[20,21] in the test medium at 25 °C by incremental addition of standard aq. KOH or HCl to 100 ml of 50% v/v 0.1M-KCl–ethanol in a thermostatted titration cell. From the measured pH and the calculated $[H^+]$ at each datum point, the calibration relationship $pH_m = Mp[H^+] + C$ was derived using $p[H^+]$ data in the range 1.7—4.0 and 10.0—12.0. The value of M (1.003 to 1.046) and C (0.43 to 0.32) varied slightly with the electrode pair used.

In a typical titration ethanol (50 ml) was added to *ca.* 3.5×10^{-3} mol of compound in the titration vessel. After dissolution aqueous 0.2M-KCl (50 ml) was added slowly, followed by ethanol equal to half the calculated volume of standard alkali required for titration of the acid (*ca.* 0.5 ml). The solution was flushed with N_2 (equilibrated over the test medium at 25 °C) to remove CO_2 (30 min) before incremental addition of aqueous KOH (Gilmont micrometer syringe). The electrode pair was standardised against the NBS buffers before and after each titration (after 30 min soaking in distilled water); all pH_m values were corrected for any electrode drift.

The value of the concentration quoted K_c $\{= ([HA]_0 - [HA]_i + [H^+]_i)[H^+_i]/([HA_i] - [H^+]_i)\}$ was calculated at each of the 12—20 datum points in the buffer region, n_H = 0.2—0.7 (where n_H is the average number of protons bound to the conjugate base A^-). The 'pK_a' $(= pH_m - \log [A^-]_i/[HA]_i)$ values, which cannot be calculated directly from the mass balance equations, were obtained from the relationship $K_a = 10^{-pHm}$ m $K_c/10^{-p[H^+]}$. The values reported in Table 2 are the mean ±s.d. from either two or three titrations.

Aqueous KOH was prepared in CO_2-free double deionised (Mili-Q) water from the Analar reagent, and standardised against potassium hydrogen phthalate. Ethanol was purified by refluxing over calcium oxide for 10 h followed by distillation from magnesium ethoxide.

Kinetic Measurements.—The rates of solvolysis were followed by means of a pH-stat, the method being based on that used of Fischer and co-workers for 2-(1-pyridyl)propan-2-yl chlorides.[22] The 2-propyl chloride (in an amount calculated to require less than 1 ml of 0.1M-NaOH) was added to the acetone–water solution (50—60 ml) in a jacketed cell containing both a glass and a calomel electrode, a mechanical stirrer, and the

Table 2. Dissociation constants of benzoic and phenylacetic acids in 50% ethanol[a]

(*a*) Benzoic acids

Substituent	pK_a	Substituent	pK_a
H	5.49	3-PhN_2	5.11
3-Me	5.64	4-PhN_2	5.02
3-F	5.07	3-Bu^tN_2	5.17
3-Cl	5.02	4-Bu^tN_2	5.11
3-NO_2	4.44	4-(2′,6′-$Me_2C_6H_3$)N_2	5.07
4-Cl	5.14		
4-NO_2	4.35		
3,5-$(NO_2)_2$	3.42		

(*b*) 3,5-Dimethylbenzoic acids

H	5.68	4-PhN_2	5.44
4-MeO	5.71	4-Bu^tN_2	5.49
4-Cl	4.35	4-(2′,6′-$Me_2C_6H_3$)N_2	5.49
4-CN	4.65		

(*c*) Phenylacetic acids

H	5.47	4-PhN_2	5.22
3-Me	5.53	4-Bu^tN_2	5.27
3-F	5.26		
3-Br	5.26		
3-NO_2	4.92		
4-Cl	5.27		

[a] The pK_a values listed are those applying in 50% v/v ethanol–water at 25 °C. The solution was 0.1M in KCl.

Table 3. Summary of rate constants for the solvolysis of $XC_6H_4CMe_2Cl$ in aqueous acetone at 25 °C

	$k \times 10^4/s^{-1}$		
X	87.5% Acetone	80% Acetone	72.5% Acetone
4-Bu^t	39.3		
3,5-diMe	10.3		
4-F	7.57	43.1	
3-Me	7.04	38.3	
H	2.94	20.8	
4-Cl		6.33	19.5
4-Br		5.05	14.3
4-PhN_2		4.02	11.3
4-Bu^tN_2			14.3
4-(4′-$MeOC_6H_4$)N_2		16.0	
4-(4′-MeC_6H_4)N_2			16.1
4-(4′-FC_6H_4)N_2			10.6
4-(4′-BrC_6H_4)N_2			7.99
4-(3′-BrC_6H_4)N_2			5.71
4-(2′,6′-$Me_2C_6H_3$)N_2			10.1
3,5-Me_2-4-$C_6H_2N_2$	8.75		
4-Bu^t-3,5-$Me_2C_6H_2N_2$	33.9		
3,5-Me_2-4-(2′,6′-$Me_2C_6H_3N_2$)	10.1		

Table 4. Hammett substituent constants for arylazo and t-butylazo[a] groups

Substituent	σ_m	σ_p^0	σ_p	σ_p^+	σ_p[b]	σ_p^+[b]
Phenylazo	+0.28	+0.37	+0.34	+0.17	+0.18	+0.01
4′-Methoxyphenylazo				+0.03		
4′-Methylphenylazo				+0.13		
4′-Fluorophenylazo				+0.18		
4′-Bromophenylazo				+0.21		
3′-Bromophenylazo				+0.24		
2′,6′-Dimethylphenylazo			+0.31	+0.18	+0.14	0.00
t-Butylazo	+0.24	+0.30	+0.28	+0.15	+0.14	−0.13

[a] Details of the method used to evaluate the substituent constants are given in the text. [b] These values represent estimates for σ_p and σ_p^+ for the conformation adopted by the substituent when there are methyl groups in the 3- and 5-positions. They have been corrected for the presence of these by subtracting 0.13 from the original values obtained.

syringe needle. Water from a thermostatted water bath (T = 25 °C) was circulated through the jacket. The pH was maintained at 6.0 by addition of 0.1M-NaOH, with the volume of base used being recorded. Near the end of the reaction the titration was completed manually to determine the endpoint volume of base. At the start of each day the electrodes were standardised using borax buffer. Between each run the electrodes were soaked in distilled water for 20—40 min. In practice only rates with half-lives in a limited range could be measured accurately. Because of the range of reactivities involved, three solvent systems (87.5%, 80%, and 72.5% v/v acetone–water) had to be used. The first-order rate constants were calculated from the slope of plots of log $(V_\infty - V_t)$ against time, t. These plots were linear over at least 70% of the reaction. The rate constants reported in Table 3 are mean values based on several runs and are considered reliable to ±5%.

Calculation of σ^0-, σ-, *and* σ_p^+-*Values.*—All substituent constants were calculated using ρ-values determined from the results obtained using derivatives for which these were known. Our ρ-values for the benzoic acids (+1.43) and phenylacetic acids (+0.72) may be compared with those reported by Wepster (+1.516 and +0.74).[23] The variations represent differences in the choice of substituents used to define ρ rather than the pK_a values themselves.

For the solvolysis reaction ρ-values of −4.24 and −4.21 were obtained for 87.5% acetone and 80% acetone respectively. For 72.5% acetone σ_p^+ constants were calculated by assuming a ρ-value of −4.22, with the line passing through a point midway between the values for *p*-Cl and *p*-Br. This yielded a value for *p*-phenylazo identical to that obtained in 80% acetone.

Because the range of σ and σ_p^+ constants obtained corresponded closely to those of the standards used, and because none proved to have either high negative or high positive values, we believe they may be considered reliable to ±0.03. In the case of the σ^0-values, the low ρ-value for the phenylacetic acid ionisation reaction is likely to lead to the possibility of greater deviations, and for these ±0.05 might be more appropriate.

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