Cross-interaction Constants as a Measure of the Transition-state Structure. Part 1. The Degree of Bond Formation in Nucleophilic Substitution Reactions

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The kinetics of seven reaction series in methanol involving halides as leaving groups and aromatic amines as nucleophiles are reported. Analyses of various Hammett ρ values, especially the cross-interaction constants ρ_{XY} between substituents X in the nucleophile and Y in the substrate, are used to characterize the transition-state structure for the nucleophilic substitution reactions. The degree of bond formation in the transition state as measured by $|\rho_{XY}|$ indicated that the reactions can be classified into two groups according to the magnitude of the cross-interaction constants; the fluoride series gave larger $|\rho_{XY}|$ values indicating a greater degree of bond formation, under the same reactants condition, compared with other series with relatively good leaving groups, *e.g.* Cl^-, Br^-, and $^-OSO_2C_6H_5$. When, however, a non-conjugative intervening group such as CO or CH_2 is present between the reaction centre and the benzene ring of a reactant, the cross-interaction constant is reduced by a factor of *ca.* 2, demonstrating the fall-off of the susceptibility of the reaction centres to substituent changes.

The magnitude of Hammett ρ values has long been used as a means of assessing relative bond tightness in the transition state (TS). However, it has often been pointed out that the efficiency of charge transmission between reaction centres R_X, R_Y, and R_Z (Scheme) in bond formation or cleavage may differ for different reaction series[1] so that $|\rho_i|$ (i = X, Y, or Z) can at most serve as a relative measure of bond lengths r_{XY} or r_{YZ} within a particular family of closely related reactions.[1,2] In contrast, the magnitude of cross-interaction constants, *e.g.* $|\rho_{XY}|$ in equation (1), reflects

$$\log (k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (1)$$

the intensity of indirect interaction between substituents X and Y through reaction centres R_X and R_Y when both substituents interact with their respective reaction centres simultaneously in the TS, and provides a useful quantitative measure of bond length r_{XY}.[3] It has been shown that r_{XY} is linearly related to logarithm $(|\rho_{XY}|^{-1})$ [equation (2)[4] where α and β are constants

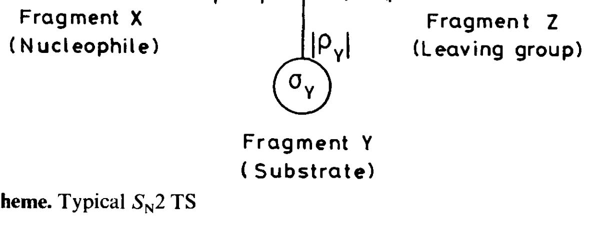
$$r_{XY} = \alpha + \beta \log (|\rho_{XY}|^{-1}) \qquad (2)$$

which depend on the rows of the Periodic Table for the two atoms being bonded at constant temperature].[5] On the other hand, the bond length r_{XY} has been shown to vary linearly with the Hammett substituent constant, σ_Z, in the leaving group (LG) [equation (3)[6]] which leads to yet another useful correlation (4).[6] In equations (3) and (4) λ and k are negative and positive constants respectively, for a kinetically controlled reaction series,[7] whereas the signs reverse to $\lambda > 0$ and $k < 0$ for a thermodynamically controlled reaction series.[7] Equations (3) and (4) indicate that for a kinetically controlled series a

$$\Delta r_{XY} = \lambda\sigma_Z \qquad (3)$$

$$\Delta\log|\rho_{XY}| = k\sigma_Z \qquad (4)$$

better LG with a more electron-withdrawing substituent (EWS), $\sigma_Z > 0$, gives a shorter r_{XY} *i.e.*, a greater degree of bond formation, with a greater value of $|\rho_{XY}|$, which is consistent with the prediction of the variations of TS by a quantum mechanical (QM) model.[8] In contrast, for a thermodynamically controlled reaction series a more EWS in the LG, $\sigma_Z > 0$, should lead to a greater r_{XY}, *i.e.*, a smaller degree of bond formation, with a smaller value of $|\rho_{XY}|$, which is in agreement with the prediction based on the potential energy surface (PES) model.[8,9]



Scheme. Typical S_N2 TS

Table 1. Second-order rate constants, k_2/l mol^{-1} s^{-1}, and Hammett reaction constants for the reactions of YC_6H_4COCl with $XC_6H_4NH_2$ in methanol at 35.0 °C

X\Y	*p*-CH_3	H	*p*-Cl	ρ_Y[a]
p-CH_3	82.6	212	726	2.36
H	30.0	81.8	219	2.14
p-Cl	10.2	23.7	60.8	2.14
m-NO_2	1.06	2.20	5.25	1.74
ρ_X[a]	−2.12	−2.25	−2.39	

[a] Correlation coefficient ⩾ 0.995.

In this paper we present some examples to demonstrate that the degree of bond formation, as measured by the magnitude of ρ_{XY}, is similar for a class of similar reactions, so that $|\rho_{XY}|$ provides a quantitative measure of the bond length r_{XY} in the TS of nucleophilic substitutions.

Results and Discussion

Second-order rate constants k_2 for the reactions of benzoyl chlorides and fluorides with anilines are summarized in Tables 1

Table 2. Second-order rate constants, $10^3\,k_2$/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of YC_6H_4COF with $XC_6H_4NH_2$ in methanol at 55.0 °C

X\Y	*p*-CH_3	H	*p*-Cl	ρ_Y[a]
p-OCH_3	90.1	178	688	2.23
p-CH_3	33.2	74.1	198	1.93
H	13.0	22.0	63.0	1.73
p-Cl	2.90	4.79	10.0	1.35
σ_X[a]	−2.89	−3.11	−3.55	

[a] Correlation coefficient ⩾ 0.994.

Table 3. Second-order rate constants, 10^4k_2/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of $YC_6H_4SO_2F$ with $XC_6H_4NH_2$ in methanol at 45.0 °C

X\Y	*p*-OCH_3	*p*-CH_3	H	*p*-Cl	*p*-NO_2	ρ_Y[a]
p-OCH_3	2.29	3.51	6.38	13.3	76.7	1.43
p-CH_3	1.88	2.68	4.61	9.14	48.4	1.33
H	1.22	1.70	2.66	5.03	20.3	1.15
p-Cl	0.747	0.927	1.33	2.30	6.53	0.90
ρ_X[a]	−0.99	−1.15	−1.36	−1.52	−2.15	

[a] Correlation coefficient ⩾ 0.999.

Table 4. Second-order rate constants, k_2/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of $YC_6H_4SO_2Cl$ with $XC_6H_4CH_2NH_2$ in methanol at 35.0 °C

X\Y	*p*-OCH_3	*p*-CH_3	H	*p*-Cl	*p*-NO_2	ρ_Y[a]
p-OCH_3	1.99	3.11	5.75	13.3	103	1.62
p-CH_3	1.55	2.30	4.17	9.78	70.8	1.58
H	0.973	1.37	2.30	5.51	37.9	1.52
p-Cl	0.491	0.682	1.09	2.42	15.1	1.42
ρ_X[a]	−1.22	−1.32	−1.45	−1.49	−1.67	

[a] Correlation coefficient ⩾ 0.999.

Table 5. Second-order rate constants, 10^3k_2/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of $YC_6H_4SO_2F$ with $XC_6H_4NH_2$ in methanol at 45.0 °C

X\Y	*p*-OCH_3	*p*-CH_3	H	*p*-Cl	*p*-NO_2	ρ_Y[a]
p-OCH_3	3.31	4.07	5.75	9.33	28.8	0.90
p-CH_3	2.88	3.55	4.84	7.41	20.4	0.81
H	2.26	2.75	3.63	5.25	12.6	0.71
p-Cl	1.66	1.91	2.34	3.16	6.38	0.56
ρ_X[a]	−0.60	−0.66	−0.78	−0.93	−1.30	

[a] Correlation coefficient ⩾ 0.997.

Table 6. Second-order rate constants, 10^3k_2/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of $YC_6H_4CH_2Br$ with $XC_6H_4CH_2NH_2$ in methanol at 45.0 °C

X\Y	*p*-CH_3	H	*p*-Cl	*p*-NO_2	ρ_Y[a]
p-OCH_3	20.0	14.5	12.6	7.94	−0.36
p-CH_3	13.8	10.5	9.12	5.40	−0.37
H	10.0	6.92	5.65	3.02	−0.47
p-Cl	6.03	3.63	3.02	1.52	−0.52
ρ_X[a]	−1.00	−1.19	−1.23	−1.43	

[a] Correlation coefficient ⩾ 0.997.

Table 7. Second-order rate constants, 10^2k_2/l mol^{-1} s^{-1}, and Hammett coefficients for the reactions of $YC_6H_4COCH_2Br$ with $XC_6H_4CH_2NH_2$ in methanol at 45.0 °C

X\Y	H	*p*-Cl	*p*-NO_2	ρ_Y[a]
p-OCH_3	3.72	4.50	10.6	0.36
p-CH_3	2.96	3.69	8.69	0.37
H	2.12	2.59	6.38	0.38
p-Cl	1.33	1.67	4.18	0.39
ρ_X[a]	−0.89	−0.86	−0.81	

[a] Correlation coefficient ⩾ 0.999.

and 2 together with the simple Hammett ρ values for substituent changes in both the nucleophile, ρ_X, and the substrate, ρ_Y. Likewise the results of rate studies on the reactions of benzenesulphonyl fluorides with anilines are given in Table 3, and those on the reactions of benzenesulphonyl chlorides and fluorides with benzylamines are presented in Tables 4 and 5.

Reference to Tables 1—5 reveals that the rates are *ca.* 10^3 times faster for chloride series than those for the corresponding fluoride series, but the reactivity trends are the same for all series; a more electron-donating substituent (EDS) in the nucleophile ($\sigma_X < 0$) and a more EWS in the substrate ($\sigma_Y > 0$) lead to a higher rate with greater magnitudes of ρ_Y (>0) and ρ_X (<0), indicating a larger degree of bond formation. The positive ρ_Y values for these series imply more charge transfer from the nucleophile, and hence a larger degree of bond formation, than the charge carried away by the LG, *i.e.*, bond breaking in the TS.

The results of rate studies on the reactions of benzylamines with benzyl and phenacyl bromides are summarized in Tables 6 and 7, respectively. These two series of reactions have different reactivity and/or selectivity trends from those of the series in Tables 1—5 and also from each other. For benzyl bromides, the reactivity is higher for a more EDS in the nucleophile as well as in the substrate with negative ρ_X and ρ_Y values, but the magnitudes of both ρ_X and ρ_Y increase with a more EWS in both the substrate and the nucleophile. The negative ρ_Y values for this series indicate more advanced bond breaking than bond formation in the TS.

In contrast, for the phenacyl bromides the reactivity trends and the signs of all the ρ values agree with those of the series in Tables 1—5; a higher reactivity is obtained with a more EDS in the nucleophile and with a more EWS in the substrate, with $\rho_X < 0$ and $\rho_Y > 0$. However, the selectivity trends are quite contrary to those for the reaction series in Tables 1—5; a more EWS, in the nucleophile, leads to an increase in $|\rho_Y|$, whereas in the substrate, it leads to a decrease in $|\rho_X|$. This means that for the phenacyl bromides series the reactivity–selectivity principle[10] is valid. In fact, the phenacyl series is in general known to give thermodynamic control and all the thermodynamically based rules or principles hold.[7]

Results of ρ_{XY} values determined by multiple regression analysis[11] using equation (1) are collected in Table 8[12—23] together with those obtained from other sources. The Hammett coefficients, ρ_X and ρ_Y, in Table 8 agree well with the corresponding values obtained by the simple linear Hammett plots in Tables 1—7. All except reaction G in class I involve anilines as nucleophiles and LGs of relatively good leaving ability, Cl^-, Br^-, and $C_6H_5O_2SO^-$. A striking feature for the class I reactions is that the cross-interaction constants, ρ_{XY}, which are negative, have a similar magnitude, $|\rho_{XY}|$ 0.70 ± 0.08. Reactions in this class are considered to be good examples of the S_N2 type, and the similar size of ρ_{XY}, therefore, provides evidence in support of a similar degree of bond formation, r_{XY}, in the TS.

Close examination of the ρ_X values, however, reveals that the magnitude varies widely, $|\rho_X|$ 0.58—2.24, in contrast to the relatively constant $|\rho_{XY}|$ values. This is a clear demonstration of variable charge transmission[1] reflected in $|\rho_X|$, depending on the reaction centres R_X and R_Y in the Scheme, although in reality a

Table 8. Results of multiple regression analysis[11] of the rate constants k_2, using $\log (k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y$, where X and Y are the substituents in the nucleophile and substrate, respectively

Class		Reactions	ρ_X	ρ_Y	ρ_{XY}	Correlation coefficients	Ref.
I	A	$XC_6H_4NH_2 + YC_6H_4COCl \xrightarrow[35.0\,°C]{MeOH}$	−2.24	2.17	−0.68	0.999	This work
	B	$XC_6H_4NH_2 + YC_6H_4CH_2Cl \xrightarrow[50.0\,°C]{EtOH}$	−0.98	−0.61	−0.77	0.974	12
	C	$XC_6H_4NH_2 + YC_6H_4SO_2Cl \xrightarrow[35.0\,°C]{MeOH}$	−2.14	0.96	−0.70	0.998	13
	D	$XC_6H_4NH_2 + YC_6H_4SO_2Cl \xrightarrow[25.0\,°C]{MeOH}$	−2.15	1.10	−0.75	0.997	14
	E	$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z \xrightarrow[35.0\,°C]{MeOH}$	−0.92	−0.75	−0.62	0.999	15
	F	$XC_6H_4NH_2 + YC_6H_4CH_2Br \xrightarrow[35.0\,°C]{MeOH}$	−1.33	−0.67	−0.78	0.991	16
	G	$XC_6H_4S^- + YC_6H_4CH_2Cl \xrightarrow[20.0\,°C]{MeOH}$	−0.58	0.58	−0.62	0.982	17
II	H	$XC_6H_4NH_2 + YC_6H_4COF \xrightarrow[55.0\,°C]{MeOH}$	−3.14	1.72	−1.67	0.997	This work
	I	$XC_6H_4NH_2 + YC_6H_4SO_2F \xrightarrow[45.0\,°C]{MeOH}$	−1.31	1.15	−1.07	0.999	This work
III	J	$XC_6H_4NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow[45.0\,°C]{MeOH}$	−1.97	0.61	0.11	0.999	18
	K	$XC_6H_4NH_2 + YC_6H_4COCH_2Br \xrightarrow[45.0\,°C]{MeOH}$	−1.81	0.61	0.11	0.999	19
	L	$XC_6H_4NH_2 + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow[60.0\,°C]{MeOH}$	−1.22	−0.15	−0.12	0.999	20
IV	M	$XC_6H_4CH_2NH_2 + YC_6H_4SO_2Cl \xrightarrow[35.0\,°C]{MeOH}$	−1.38	1.51	−0.39	0.999	This work
	N	$XC_6H_4CH_2NH_2 + YC_6H_4CH_2Br \xrightarrow[45.0\,°C]{MeOH}$	−1.15	−0.46	−0.38	0.997	This work
	O	$XC_6H_4CH_2NH_2 + YC_6H_4SO_2F \xrightarrow[45.0\,°C]{MeOH}$	−0.78	0.71	−0.66	0.999	This work
V	P	$XC_6H_4CH_2NH_2 + YC_6H_4COCH_2Br \xrightarrow[45.0\,°C]{MeOH}$	−0.88	0.37	0.05	0.999	This work
	Q	$XC_6H_4CH_2NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow[45.0\,°C]{MeOH}$	−0.74	0.54	0.03	0.999	21
	R	$XC_6H_4CHCHCO_2^- + YC_6H_4COCH_2Br \xrightarrow[35.0\,°C]{9:1\ Me_2CO–H_2O}$	−0.22	1.07	−0.04	0.988	22
	S	$(XC_6H_4)_2\text{–}C\text{–}N{\equiv}N + YC_6H_4CO_2H \xrightarrow[34.9\,°C]{C_6H_5CH_3}$	−1.70	2.22	−0.09	0.999	23

similar degree of bond formation, *i.e.*, a similar value of r_{XY}, is involved in the TS of the reactions in this class, as the similar $|\rho_{XY}|$ values indicate.

The LG for reactions in class II is fluoride and, as for reactions in class I, ρ_X and ρ_{XY} are both negative. However, a notable difference between the reactions in the two classes is the size of ρ_{XY}, which is greater for the fluoride series by more than 1.5 times that of the corresponding series with chloride LG in class I. It is well known that fluoride is a much worse LG compared with chloride due to the weak electron-accepting ability of the C–F or S–F bond.[24] The greater $|\rho_{XY}|$ values for class II reactions indicate that a worse LG leads to a greater degree of bond formation, which is consistent with the predictions of the TS variation by the PES model. This may be due to the dominant influence of the thermodynamic driving force or barrier to reactivity, since the change of the LG from Cl^- to F^- involves a large pK_a change, *i.e.*, from $pK_a(Cl^-)$ −5.7 to $pK_a(F^-)$ 3.45 (ΔpK_a *ca.* 9.0).[25]

Comparison of reactions C and I indicates that $|\rho_X|$ is small for I despite the large $|\rho_{XY}|$ value, supporting our previous conclusion[26] on the unreliability of the Hammett ρ_X value as a measure of bond tightness due to the variable charge transmission.

Reactions in classes I and II are characterized by negative ρ_X and ρ_{XY} values, reflecting rate-limiting nucleophilic bond formation ($\rho_X < 0$), in which a more EWS in the substrate ($d\sigma_Y > 0$) leads to a greater degree of bond formation ($d\rho_X < 0$) [relationship (5)]. For reactions in class II, the

$$\rho_{XY} = \partial\rho_X/\partial\sigma_Y < 0 \qquad (5)$$

possibility of an S_AN mechanism[27] cannot be entirely ruled out, but the rate-determining step should still be addition since rate-limiting elimination would require a negligible $|\rho_{XY}|$ value,[3] *i.e.*, $|\rho_{XY}|$ *ca.* 0.

The variation in TS with substituent changes for reaction E has been shown to be consistent with predictions by the QM model;[15] the constant k [equation (4)] was found to be positive and hence λ [equation (3)] should be negative, so that a greater degree of bond formation is obtained with a more EWS ($\sigma_Z > 0$) in the LG. For this reaction series, all three ρ factors, *i.e.*, ρ_X, ρ_Y, and ρ_{XY}, are negative, which provide a necessary condition for a kinetically controlled reaction series.

Substrates for reactions in class III are phenacyl and 2-phenylethyl derivatives. For the phenacyl systems, ρ_{XY} is positive in contrast to those for the other reaction series in Table 8. For reaction J, a more EWS in the LG ($\sigma_Z > 0$) resulted in a decrease in ρ_{XY},[18] and hence k is negative and λ positive. This is the opposite trend to that found for reaction E,[15] but in agreement with predictions by the PES model and provides an example of a thermodynamically controlled reaction series. For this series, both ρ_Y and ρ_{XY} are positive, which constitutes a necessary condition for a thermodynamically controlled reaction series. For reactions of 2-phenylethyl series, however, the sign of ρ_{XY} is negative and moreover k was found to be positive[26] and hence λ negative.

It is to be noted that the magnitudes of ρ_{XY} for the phenacyl and 2-phenylethyl series are small but nearly the same (*ca.* 0.11), despite the opposite signs of ρ_{XY}. One reason why such smaller $|\rho_{XY}|$ values are obtained relative to those in class I ($|\rho_{XY}|$ *ca.* 0.70) may be an intervening CO or CH_2 group in the substrate between the reaction centre carbon and the benzene ring, since a non-conjugative intervening group is known to reduce the susceptibility of the reaction centre to substituent changes, *i.e.*, $|\rho|$, by approximately a factor of two.[28] However even after allowing for the decrease due to an intervening group, the size of $|\rho_{XY}|$ for reactions in class III is still much smaller. For the phenacyl series, resonance shunt or electron leak to the intervening α-carbonyl group has been proposed,[18] while for the 2-phenylethyl series aryl participation has been suggested[20] to explain the unusually low values of $|\rho_{XY}|$.

In classes IV and V, the nucleophile changes to benzylamine and other amines. Benzylamine is more basic than aniline, ΔpK_a *ca.* 5.0,[29] and hence is a stronger nucleophile, but it has an extra intervening CH_2 group between the reaction centre and the ring. We note that the magnitudes of ρ_{XY} for reactions M—O are slightly greater than half those for the corresponding reactions with aniline in classes I and II, but the signs of ρ_X, ρ_Y, and ρ_{XY} agree. Comparison of reactions M, N, and O again shows that $|\rho_{XY}|$ is greater for the fluoride series (reaction O) than those for the chloride and bromide series (reactions M and N), although $|\rho_X|$ is smaller for the fluoride series. We would have expected a greater degree of bond formation, and hence a greater $|\rho_{XY}|$ value, with benzylamine, since it is a stronger nucleophile than aniline. However, it appears that cross interaction between the substituents X in the nucleophile and Y in the substrate is reduced by a factor of two due to an intervening non-conjugative CH_2 group in benzylamine, albeit bond formation may be somewhat greater. This argument also applies to the phenacyl series with benzylamine in class V, since here again the signs agree with those of the corresponding reactions in class III but the size has reduced to a little less than half.

The anionic nucleophile in reaction R,[22] $XC_6H_4CH{=}CH{-}CO_2^-$, seems to alter the nature of the reaction since the sign of ρ_{XY} is now negative even though the substrate is the same phenacyl compound. A conjugative intervening group $CH{=}CH_2$ in the nucleophile seems to have little effect on the size of $|\rho_{XY}|$.

The last reaction series, S[23] has a little larger $|\rho_{XY}|$ than expected probably due to the two-fold interaction between the two identical substituents X in the two phenyl groups and the substituent Y in the substrate acid.

Experimental

Material.—Anilines were purified by distillation or crystallization, Fluka purum grade benzylamines were purified by distillation: b.p.s were; $C_6H_5CH_2NH_2$, 92—94 °C at 15 mmHg (lit.,[30] 70—71 °C at 10 mmHg); *p*-$CH_3OC_6H_4CH_2NH_2$, 110—114 °C at 15 mmHg; *p*-$CH_3C_6H_4CH_2NH_2$, 80—82 °C at 12 mmHg; *p*-$ClC_6H_4CH_2NH_2$, 95—97 °C at 12 mmHg. GR grade methanol was without further purification. GR grade benzoyl chlorides (Tokyo Kasei) were purified by distillation: b.p.s were: C_6H_5COCl, 83 °C at 12 mmHg; *p*-$CH_3C_6H_4COCl$, 99 °C at 12 mmHg; *p*-ClC_6H_4COCl, 102—105 °C at 15 mmHg. Benzoyl fluorides were prepared[31] from benzoyl chlorides as follows. Benzoyl chloride (0.59 g, 0.0036 mol) was stirred with 18-crown-6-ether (5 mol %) in a round-bottomed flask adding KF successively to excess. After 4 h, the reactants were transferred to a separating funnel and KCl formed and unchanged KF were dissolved by adding distilled water. The organic layer was then extracted with ether, which was then evaporated, leaving the product (yield 75—80%). After distillation the products had b.p.s 67—68 °C at 10 mmHg (*p*-$CH_3C_6H_4COF$), 43—45 °C at 10 mmHg (C_6H_5COF), and 63—65 °C at 10 mmHg (*p*-ClC_6H_5COF). The results of spectroscopic and elemental analyses are as follows.

p-$CH_3C_6H_4COF$, $\nu_{max.}$(neat) 1 750 (C=O, sym. str.), 1 300 ($C_6H_4CH_3$), 1 050 (C–F, str.), and 790 cm^{-1} (C_6H_4, *para* subs.); δ (60 MHz; $CDCl_3$) 7.0—7.3 (2 H), 7.8—8.0 (2 H), and 2.4 (3 H) (Found: C, 69.4; H, 5.1. Calc. for C_8H_7FO: C, 69.6; H, 5.1%).

C_6H_5COF, $\nu_{max.}$(neat)[32] 1 750 (C=O, str.), 1 010 (C–F, str.), and 770 and 700 cm^{-1} (C_6H_5, mono subs.); δ (60 MHz; $CDCl_3$) 7.2—7.7 (3 H) and 7.8—8.2 (2 H) (Found: C, 67.7; H, 4.0. Calc. for C_7H_5FO: C, 67.7; H, 4.0%).

p-ClC_6H_4COF, $\nu_{max.}$(neat) 1 750 (C=O, sym. str.), 1 070 (C–F, str.), and 800 cm^{-1} (C_6H_4, *para* subs.); δ (60 MHz; $CDCl_3$) 7.3—7.6 (2 H) and 7.8—8.2 (2 H) (Found: C, 53.0; N, 2.6. Calc. for C_7H_4ClFO: C, 53.0; H, 2.5%).

Benzenesulphonyl fluorides were prepared[31] from chlorides as follows. Benzenesulphonyl chloride and 1 equiv. KF in dry acetonitrile were stirred for 24 h with 18-crown-6 ether (5 mol %). The product fluoride precipitated out on addition of excess of water and was recrystallized after drying. M.p.s, R_F (t.l.c.; silica gel plate; eluant 30% ethyl acetate–n-hexane) values, and spectroscopic data are as follows.

p-$CH_3C_6H_4SO_2F$, m.p. 41—43 °C (lit.,[33] 41—42 °C); R_F (0.49); $\nu_{max.}$(KBr) 1 410 (SO_2, asm. str.), 1 215 and 1 205 (SO_2, sym. str.), 1 090 (S–O, sym. str.), and 760 cm^{-1} (O_2S–F, sym. str.).

p-$CH_3OC_6H_4SO_2F$, b.p. 93—94 °C at 16 mmHg; R_F (0.32); $\nu_{max.}$ (neat) 2 840 (OCH_3, str.), 1 400 (SO_2, asym. str.), 1 210 (SO_2, sym. str.), and 760 cm^{-1} (O_2S–F, sym. str.).

$C_6H_5SO_2F$, b.p. 88—89 °C at 13 mmHg; R_F (0.52); $\nu_{max.}$(neat) 1 410 (SO_2, asym. str.), 1 210 (SO_2, sym. str.), and 1 740 cm^{-1} (O_2S–F, sym. str.).

p-$ClC_6H_4SO_2F$, m.p. 36—37 °C; R_F (0.46); $\nu_{max.}$(KBr) 1 405 (SO_2, asym. str.), 1 210 (SO_2, sym. str.), 1 085 (S–O, sym. str.), 900 (C_6H_5–Cl, sym. str.), and 740 cm^{-1} (O_2S–F, sym. str.).

p-$NO_2C_6H_4SO_2F$, m.p. 39—40 °C; R_F (0.38); $\nu_{max.}$ (KBr) 1 415 (SO_2, asym. str.), 1 210 (SO_2, sym. str.), 1 090 (S–O, sym. str.), 910 (C_6H_5–NO_2, sym. str.), and 730 cm^{-1} (O_2S–F, sym. str.).

Phenacyl bromides (Tokyo Kasei GR grade) were used after recrystallization from ethanol. M.p.s ($YC_6H_4COCH_2Br$) are: Y = H, 52—53 °C (lit.,[34] 49.5—50 °C); Y = *p*-Cl, 96—98 °C (lit.,[35] 96—97 °C); Y = *p*-NO_2, 98—99 °C.

Kinetic Procedures.—Second-order rate constants were determined conductometrically, under pseudo-first-order conditions, following the procedure already described,[17] except for the fast reaction series. We have devised an automated conductivity bridge system, in which the treatment of the conductivity data is computerized. In this system, 16 channels (bridges) can be used at a time and data points can be taken at time intervals ranging from 0.5 to 64 000 s so that relatively fast reactions, k_2 *ca.* 10^2 l mol^{-1} s^{-1}, can be easily handled. Pseudo-first-order rate constants from Guggenheim plots of the conductivity data were found to agree within ±4% of the value obtained by the conventional method.

Product Analysis.—For the reaction of benzoyl fluoride with aniline, product analysis was performed. T.l.c. analysis of the reaction mixture gave three spots corresponding to one product at R_F 0.35 ($C_6H_5CONHC_6H_5$) and two reactants at R_F 0.28 (C_6H_5COF) and 0.20 ($C_6H_5NH_2$) using 50% ethyl acetate–cyclohexane as eluant. Results of spectroscopic and elemental analyses are: $C_6H_5CONHC_6H_5$, $\nu_{max.}$(KBr): 3 200 (NH, str.), 1 650 (C=O, sym. str.), 1 540 (CONH, str.), 1 320 (C_6H_5N, str.), and 750 and 715 cm^{-1} (C_6H_5, mono subs.); δ (60 MHz; $[^2H_6]$DMSO–$CDCl_3$) 9.5—9.9 (NH), 6.8—8.1 (5 H), and 3.1—

3.3 (NH). (Found: C, 73.9; H, 5.8; N, 6.4. Calc. for $C_{13}H_{11}NO$: C, 74.0; H, 5.8; N, 6.2%).

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