Substituent effects in nucleophiles on activation parameters in the bimolecular nucleophilic reactions in solution†

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Changes of the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, in the S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions with phenol, aniline and pyridine nucleophiles in various solvents were correlated with σ constants of the substituents in the aromatic ring of the nucleophiles. The resultant $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ reaction constants are linearly related for variations of substituents at the nucleophile. Correlation of $\delta\Delta H^{\ddagger}$ *vs.* $\delta\Delta S^{\ddagger}$ allow the estimation of the contribution of changes of the internal enthalpy, $\delta\Delta H^{\ddagger}_{\text{int}}$, to the enthalpy reaction constant, $\delta\Delta H^{\ddagger}$, which gives a single linear dependence on the Hammett ρ reaction constants for all bimolecular nucleophilic reactions. The deviations from dependence of $\delta\Delta H^{\ddagger}_{\text{int}}$ *vs.* ρ can be interpreted in terms of changes of the transition state structure or reaction mechanism. The results obtained show that the substituent effects in the nucleophiles on the charge development in the transition state are governed by the magnitude of $\delta\Delta H^{\ddagger}_{\text{int}}$.

Introduction

Bimolecular nucleophilic reactions (BNR) provide the basis for the synthesis of various classes of organic compounds. These include S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions, *etc.*[1] There is a substantial body of data on the kinetics and mechanism of these reactions.[2–10] Some generalizations of the changes in the enthalpy of activation ($\Delta H^{\ddagger}$), the entropy of activation ($\Delta S^{\ddagger}$) and the activation free energy ($\Delta G^{\ddagger}$) for BNR were made.[9,10] It was demonstrated[3,9,10] that the enthalpy and entropy of activation depend much more substantially on the reaction mechanism than the activation free energy. Hence, analysis of the main factors responsible for the ratio between the enthalpy and entropy contribution to the energy barrier for the reaction is of great importance. In this regard, studies on substituent effects in BNR have been the subject of intense interest in recent years.[2–8,10] In most cases, substituent effects are quantified by the use of the Hammett or the Hammett-like substituent constants[11,12] for aromatic systems.[13,14]

The activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ are widely used for characterizing the structures of transition states in solution BNR.[8–10,15–17] For example, it was found that solvolysis of benzyl- and benzhydryl halides follows the S_N2 and S_N1 mechanism, respectively, as S_N2 reactions show more negative values of $\Delta S^{\ddagger}$.[18] The activation parameters are also useful in proving the elimination–addition (E–Ad_N) mechanism of S_NV reactions.[19] In two-step substitution reactions of carbonyl compounds, the values of $\Delta S^{\ddagger}$ allow one to identify the rate-limiting step.[20–22]

It is known that the substituent effect $\rho\sigma$ in the framework of the general Hammett equation can be separated into enthalpic and entropic contributions.[23,24] Such a separation was made for both the σ substituent constants[25–27] and the ρ reaction constants.[23,24,28–36] Separate consideration of enthalpic and entropic contributions to the effects of substituents is useful for obtaining more conclusive information about the structure of the transition state, its connection with the ρ value and the interactions with the environment.[11,28–41] Besides, the separation of the substituent effects into enthalpic and entropic contributions is associated with the compensation effect and the isokinetic relationship.[9,10,42–46]

Earlier, the reaction constants, $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$, were determined from the dependence of the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ on the σ substituent constants for some S_N2,[28–32,47] S_NAr[36] and acyl-transfer reactions[32,35,37] [eqn (1)–(3)].

$$\Delta H^{\ddagger} = \delta\Delta H^{\ddagger}\sigma + \Delta H^{\ddagger}_0 \qquad (1)$$

$$\Delta S^{\ddagger} = \delta\Delta S^{\ddagger}\sigma + \Delta S^{\ddagger}_0 \qquad (2)$$

$$\Delta G^{\ddagger} = \delta\Delta G^{\ddagger}\sigma + \Delta G^{\ddagger}_0 \qquad (3)$$

In these equations the $\Delta H^{\ddagger}_0$, $\Delta S^{\ddagger}_0$ and $\Delta G^{\ddagger}_0$ values are the activation parameters for the unsubstituted compounds. However, in those papers[35,36,47] the changes of the reaction constants, $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$, were discussed only in the context of the single kind of reaction. A question arises of how the variations of the reaction constants, $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$, can be predicted for the different kinds of the BNR on the basis of the single equation. Convincing support for this hypothesis is derived from the consideration of Scheme 1.

This scheme shows the main mechanisms of S_N2,[2,3] S_NV,[5,19] Ad_N,[6] S_NAr[4] and acyl-transfer reactions[7] [eqn (4)–(9), Scheme 1]. For the effect of substituents on the BNR, most studies have been on the effects of structural variations in

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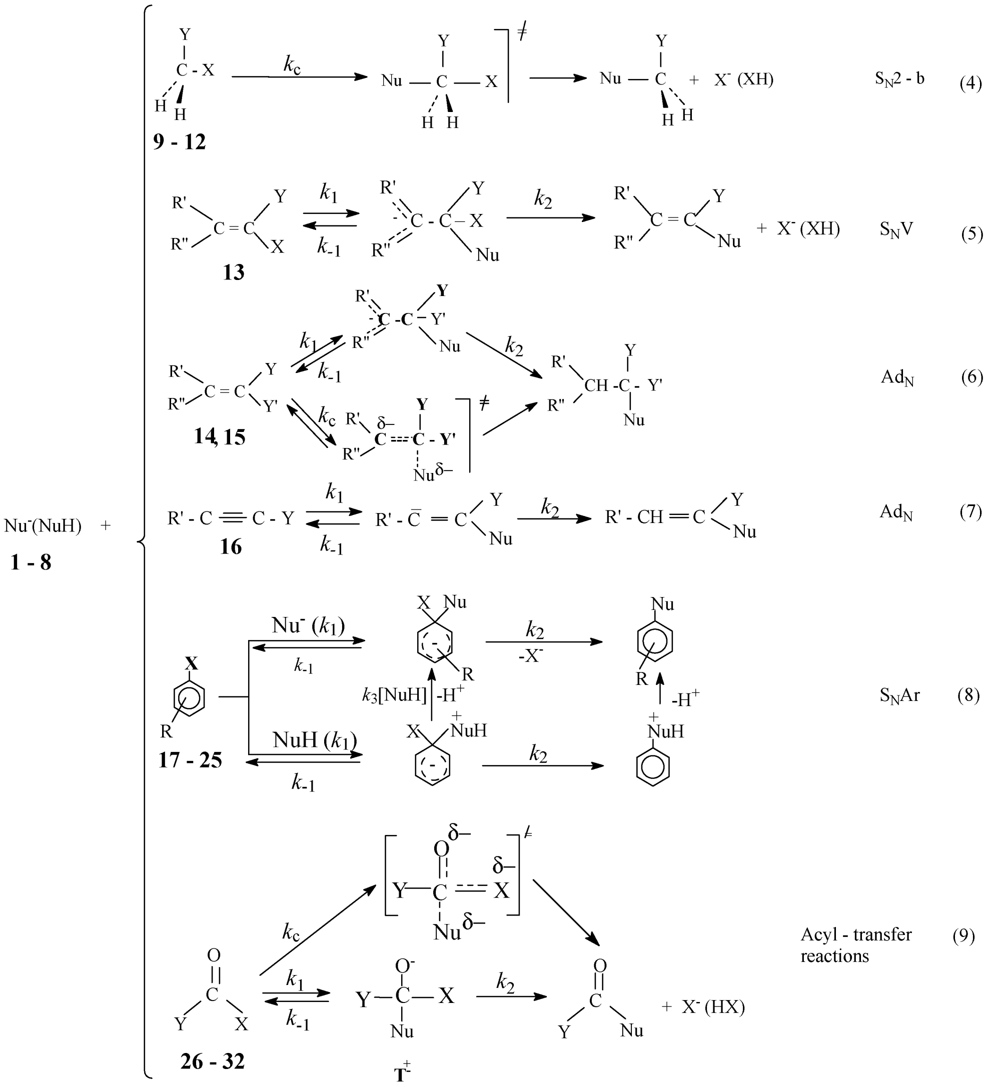
† Electronic supplementary information (ESI) available: Table S1 containing the parameters of eqn (1)–(3) for the reactions of compounds **9–32** with nucleophiles **1–8**. See DOI: 10.1039/c0nj00058b



1 NuH = $RC_6H_4NMe_2$
2 NuH = RC_5H_4N
3 NuH = $RC_6H_4NH_2$
4 Nu = $RC_6H_4S^-Na^+$
5 NuH = $RC_6H_4CH_2NH_2$
6 Nu = $RC_6H_4SH \cdot Et_3N$
7 Nu = $RC_6H_4O^-Na^+$
8 Nu = $RC_6H_4OH \cdot K_2CO_3$
9 X = I, Y = H
10 X = Br, Y = $CH_2 = CH$
11 X = Br, Y = Ph
12 X = Cl, Y = Ph
13 X = Y = Cl, R' = $PhSO_2$, R'' = H
14 Y = H, Y' = Ph, R' = R'' = CN
15 Y = H, Y' = Ph, R' = H, R'' = NO_2
16 Y = Ph, R' = C(O)Ph
17 X = Cl, Ar = 5-$NO_2C_5H_3N$
18 X = Cl, Ar = 3-$NO_2C_5H_3N$
19 X = NO_2, Ar = 3-$NO_2C_6H_4$
20 X = F, Ar = 3-$NO_2C_6H_4$
21 X = NO_2, Ar = 3-NO_2-5-CF_3-C_6H_3
22 X = F, Ar = 3-NO_2-5-CF_3-C_6H_3
23 X = F, Ar = 2,4-$(NO_2)_2C_6H_3$
24 X = Cl, Ar = 2,4-$(NO_2)_2C_6H_3$
25 X = Cl, Ar = 2,4,6-$(NO_2)_3C_6H_2$
26 X = Cl, Y = Ph
27 X = Cl, Y = PhO
28 X = Cl, Y = PhCH=CH
29 X = Cl, Y = 2-furyl-CH=CH
30 X = Cl, Y = 2-thienyl-CH = CH
31 X = Cl, Y = 3-thienyl
32 X = 2,4-$(NO_2)_2C_6H_3O$, Y = Ph

1 – 8:
a. R = 4-NH_2
b. R = 4-MeO
c. R = 4-Me
d. R =3-NH_2
e. R = 3-MeO
f. R = 3-Me
g. R = 3,4-Me_2
h. R = H
i R = 4-F
j. R = 4-Cl
k. R = 4-Br
l. R = 3-F
m. R = 3-Cl
n. R = 3,4-Cl_2
o. R = 3,5-Cl_2
p. R = 3-Br
q. R = 3-Br-5-NO_2
r. R = 4-Ac
s. R = 4-PhO
t. R = 4-Ph
u. R = 4-CF_3
v. R = 3-CF_3
w. R = 4-CN
x. R = 3-CN
y. R = 4-NO_2
z. R = 3-NO_2

Scheme 1 Reactions of compounds **9–32** with anionic and neutral nucleophiles **1–8**.

substrate and relative fewer on the nucleophile.[10,48] Furthermore, variation of the transition state structure with substituents in the nucleophile is thermodynamically controlled and the Hammett-like equation can be applied satisfactorily in this case.[16,48] It can be seen from Scheme 1 that these reactions can proceed both by concerted [eqn (4), (6) and (9)] and stepwise pathways [eqn (5)–(9)]. If in a stepwise reactions an additional step of the nucleophile to the substrate is rate-limiting [rate constant k_1 in eqn (5)–(9)], it can be supposed that the effect of the substituents R in the nucleophiles **1–8** on the changes of the reaction constants $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ can be similar for all BNR proceeding also by concerted mechanism.

The purpose of this article is to study how the substituent effect works in the nucleophile on the variations in the $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ values for typical BNR (Scheme 1). The results obtained provide a new insight into how the electronic effect of substituents in the nucleophile influences changes in the internal activation enthalpy, $\delta\Delta H^{\ddagger}_{\mathrm{int}}$, in the BNR and suggests that the development of a charge in the transition states of these reactions is mainly affected by the magnitude of $\delta\Delta H^{\ddagger}_{\mathrm{int}}$ related to the Hammett ρ reaction constants.

Methods

From the temperature-dependent rate data[9,30,35,36,47,49–71] the Eyring plots were generated by plotting $\log(k/T)$ *versus* $1/T$ and the enthalpy and entropy of activation, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, were determined for the reactions of alkyl halides **9–12**, substituted ethylenes **13–15** and acetylene **16**, substituted 2-chloro pyridines **17** and **18**, *meta*-substituted nitro-**19**, **21** and fluorobenzenes **20**, **22**, 1-fluoro- and 1-chloro-2,4-dinitro-**23**,**24** and 1-chloro-2,4,6-trinitrobenzenes **25**, acyl chlorides **26–31**, ester **32** with charged **4**, **6–8** and uncharged nucleophiles **1–3**,**5** (Scheme 1). The $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ activation parameters obtained were used by the eqn (1)–(3) to establish the $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ reaction constants (Tables 1). All details of the statistical parameters of these equations for the reactions of compounds **9–32** with nucleophiles **1–8** are given in Table S1 of the ESI.† The rate constants and the ρ values were published earlier.[9,30,35,36,49–71]

Results and discussion

The key results are summarized in Table 1. The $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ reaction constants calculated by the eqn (1)–(3) are independent on the temperature and reflect the sensitivity of the variation of activation parameters from substituent nature in the nucleophile. Whereas the $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ (or $T\delta\Delta S^{\ddagger}$) values change over a very wide range, the changes in the magnitudes of $\delta\Delta G^{\ddagger}$ occur in a narrower range for each kind of BNR. The changes of the $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values are strongly influenced by differences in solvation of reagents and transition states[32,35–37,47] The enhanced influence of solvation on the activation parameter change is characteristic of S_NAr and acyl-transfer reactions especially (entries 15–23 and 24–33 in Table 1).

For the S_N2 (entries 1–9 in Table 1), Ad_N (entries 11–13), S_NAr (entries 15–23) and acyl-transfer reactions (entries 24–33) the linear dependences between the reaction constants, $\delta\Delta H^{\ddagger}$ *vs.* $\delta\Delta S^{\ddagger}$, are supported (Table 2). For all compensation relationships presented in Table 2 the slopes and intercepts are close. The values of these parameters for the Ad_N and acyl-transfer reactions do not change a general picture of these compensation dependences. Probably this is because the reaction constants values, $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$, for the Ad_N and acyl-transfer reactions (entries 11–13 and 24–33) fall into the same range of these constants for the S_N2 and S_NAr reactions (entries 1–9, 21, 23 in Table 1). Therefore, a single linear dependence between the reaction constants, $\delta\Delta H^{\ddagger}$ *vs.* $\delta\Delta S^{\ddagger}$, for the reactions of entries 1–13, 15–33 is supported [eqn (10)] (Fig. 1). The slope of the correlation multiplied by 10^3 corresponds to a compensation temperature (*cf.* ref. 23 and 24) and is equal to 370 K.

$$\delta\Delta H^{\ddagger} = (11.8 \pm 1.3) + (0.37 \pm 0.01)\delta\Delta S^{\ddagger};$$
$$r = 0.983,\ s = 6.7,\ n = 32 \qquad (10)$$

There is the one deviation from eqn (10) which is reactions of compound **16** with nucleophiles **6** in toluene (entry 14 in Table 1, Fig. 1, Scheme 2).

These reactions are characterized by the entropy control. This is because the enthalpy of formation of nucleophiles **6** is close to the activation energy of the rate-determining step of the reaction with the rate constant k_2 *via* the transition state $\mathbf{TS_1}$ (Scheme 2). A positive value of $\delta\Delta S^{\ddagger}$ and the isoenthalpy character of the reacton are consistent with the structure of $\mathbf{TS_1}$, in which Et_3N is involved in the S–H bond cleavage (entry 14 in Table 1).[59] Of course $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ are not independent variables since changes in the former will affect the transition state structure and hence its solvation. On the other hand, the bulk of the $\delta\Delta S^{\ddagger}$ value comes from the re-solvation in going from the reagents to the transition state.[32,35–37,47,72] Therefore, for reactions of entry 14 in Table 1 the value of $\delta\Delta H^{\ddagger}$ has been calculated by eqn (10) for the reaction step leading to the transition state $\mathbf{TS_1}$ (Scheme 2).

Recently, the analysis of the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ for typical BNR revealed a number of enthalpy–entropy compensation relations depending on the reaction rate constants.[10] The chemical nature of the observed compensation relations is confirmed by the fact that the observed compensation temperatures are noticeably different from the experimental temperature range. In addition, linear relationships of $\Delta H^{\ddagger}$ *vs.* $\Delta G^{\ddagger}$ were found for these reactions.[73–76] The comparison of compensation temperature from eqn (10) with experimental ones shows a significant difference between them, and the approximate linear dependences (within the limits of errors) for the reactions of entries 1–13, 15,16, 21–33 between the $\delta\Delta H^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ values (Fig. 2) give an additional support to the chemical nature of the compensation relationship (10).[42–46,73–76]

Lines II, III and I, IV in Fig. 2 have opposite slopes due to the difference in the character of the control of the reactivity depending on the kind of BNR.[10] However, some S_NAr reactions (entries 17–20 in Table 1; Fig. 2) noticeably deviate from the line III. The reactions of entries 17–20 are characterized by the formation of the intermediate complex (**IC**) between substrates **21–24** and nucleophiles **8** before the

Table 1 Effect of substituents in nucleophiles **1–8** on activation parameters in their reactions with substrates **9–32**

Entry	Reactants	Solvent	N[a]	T/K[b]	$\delta\Delta H^{\ddagger}$/kJ mol^{-1} σ^{-1} $(r)^{c,d}$	$\delta\Delta S^{\ddagger}$/J mol^{-1} K^{-1} σ^{-1} $(r)^{c,d}$	$T\,\delta\Delta S^{\ddagger}$/kJ mol^{-1} σ^{-1}	$\delta\Delta G^{\ddagger}$/kJ mol^{-1} σ^{-1} $(r)^{c,d}$	$\delta\Delta H^{\ddagger}_{ext}$/kJ mol^{-1} σ^{-1e}	$\delta\Delta H^{\ddagger}_{int}$/kJ mol^{-1} σ^{-1f}	ρ^{c}	Ref.
S_N2 reactions												
1	$RC_6H_4NMe_2$ **1b,c,f,h,i,j,s,t** + MeI **9**	MeOH	8	328	16.4 (0.987)	7. 0	2.3	14.1 (0.995)	2.6	13.8	−2.1	30,47,49
2	$RC_6H_4NMe_2$ **1c,f,h,m,z** + MeI **9**	MeCN	5	313	10.0 (0.994)	−14.2 (0.989)	−4.4	14.4 (0.999)	−5.3	15.3	−2.43	30,47,50
3	$RC_6H_4NMe_2$ **1c,f,h,m,z** + MeI **9**	Acetone	5	313	9.8^{g} (0.997)	-15.1^{g} (0.991)	−4.7	14.6 (0.999)	−5.6	15.4	−2.40	30,47,50
4	RC_5H_4N **2h,m,o,p,w** + MeI **9**	MeCN	5	298	9.9 (0.959)	−10.7	−3.2	13.1 (0.986)	−4.0	13.9	−2.27	30,47,51
5	$RC_6H_4NH_2$ **3b,c,e,h,j** + $CH_2{=}CH{-}CH_2Br$ **10**	DMF	5	303	−20.9	−88.8 (0.968)	−26.9	6.0 (0.998)	−32.9	12.0	−1.17 $(-2.08)^{m}$	47,52
6	$RC_6H_4NH_2$ **3c,h,j,m** + $PhCH_2Br$ **11**	MeCN	4	308	−1.9	-35.4^{h} (0.995)	−10.9	9.0 (0.999)	−13.1	11.2	−1.47	47,53
7	$RC_6H_4NH_2$ **3b,c,h,j,m** + $PhCH_2Cl$ **12**	MeCN	5	318	−0.6	-25.8^{i} (0.999)	−8.5	7.9 (0.999)	−9.5	8.9	−1.23	47,53
8	$RC_6H_4NH_2$ **3c,f,h,j,k,m,n** + $PhCH_2Br$ **11**	EtOH	7	303	8.0^{j} (0.981)	7.9	2.4	5.6 (0.925)	2.9	5.1	−0.89	47,54
9	$RC_6H_4NH_2$ **3c,h,k,n,z** + $PhCH_2Br$ **11**	$PhNO_2$	5	303	7.7 (0.911)	−0.3	−0.1	7.8 (0.925)	−0.1	7.8	−1.63	47,54
S_NV reactions												
10	$RC_6H_4S^-Na^+$ **4c,h,j,y** + $PhSO_2CH{=}CCl_2$ **13**	MeOH	4	303	12.5^{k} (0.900)	37.1^{k} (0.900)	11.2	1.7^{k} (0.973)	13.7	−1.2	-0.29^{k} $(0.08)^{m}$	55
Ad_N reactions												
11	$R_6H_4H_2NH_2$ **5b–f,h–m,v,z** + $PhCH{=}C(CN)_2$ **14**	MeCN	13	293	21.8 (0.940)	48.8	14.3	7.5 (0.982)	18.0	3.7	−0.99	56
12	$RC_6H_4NH_2$ **3b–f,h,j,k,m,p,u–z** + (*E*)-$PhCH{=}CHNO_2$ **15**	MeCN	15	298	16.0 (0.940)	18.1	5.4	10.6 (0.977)	6.7	9.3	−1.88	57
13	$RC_6H_4NH_2$ **3a–f,h,j,k** + $PhC{\equiv}C{-}C(O)Ph$ **16**	95% EtOH	10	313	−3.4	−44.7 (0.930)	−14.0	10.6 (0.947)	−16.5	13.1	−2.18	58
14	$RC_6H_4SH{\cdot}Et_3N$ **6b,c,h,j,y** + $PhC{\equiv}C{-}(O)Ph$ **16**	PhMe	5	273	0 $(28.5)^{l}$	46.9^{k} (0.998)	12.8	15.7^{d}	17.3^{e}	11.2^{f}	2.52 $(-1.95)^{m}$	59
S_NAr reactions												
15	$RC_6H_4O^-Na^+$ **7b,c,f,h,j,k,v,y** + 2-Cl-5-$NO_2C_5H_3N$ **17**	MeOH	8	343	34.5 (0.974)	77.1 (0.956)	26.4	8.1	27.5	6.0	−1.2	36,60
16	$RC_6H_4O^-Na^+$ **7b,c,f,h,j,k,v,y** + 2-Cl-3-$NO_2C_5H_3N$ **18**	MeOH	8	343	34.3 (0.966)	85.0 (0.943)	29.2	5.1	31.5	2.8	−0.82	36,60
17	$RC_6H_4OH{\cdot}K_2CO_3$ **8c,g,h,j,k,y** + 1,3-$(NO_2)_2C_6H_4$ **19**	DMF	6	423	$-77.2\ (0.999)^{k}$	$-213.6\ (1.000)^{k}$	−90.4	13.2	−79.1	1.9	−1.64 $(-0.43)^{m}$	36,61,62
18	$RC_6H_4OH{\cdot}K_2CO_3$ **8c,h,j,y** + 3-$NOC_{26}H_4F$ **20**	DMF	4	423	$-86.3\ (0.999)^{k}$	$-238.1\ (0.999)^{k}$	−100.7	14.4	−88.1	1.8	−1.84 $(-0.41)^{m}$	36,61,62
19	$RC_6H_4OH{\cdot}K_2CO_3$ **8c,h,j,k,q,r,w,y** + 1,3-$(NO_2)_2$-5-$CF_3C_6H_3$ **21**	DMF	8	343	$-63.7\ (0.999)^{k}$	$-202.0\ (0.999)^{k}$	−69.3	5.6	−74.7	11.0	−0.88 $(-1.92)^{m}$	36,61,62
20	$RC_6H_4OH{\cdot}K_2CO_3$ **8c,h,j,q,r,w,y** + 3-NO_2-5-CF_3–C_6H_3F **22**	DMF	7	343	$-123.3\ (0.977)^{k}$	$-381.5\ (0.978)^{k}$	−130.8	7.6	−141.2	17.9	−1.01 $(-3.05)^{m}$	36,61,62
21	$RC_6H_4NH_2$ **3f,h,j,k,m,p** + 2,4-$(NO_2)_2C_6H_3F$ **23**	EtOH	6	303	$21.0\ (0.998)^{k}$	−9.1	−2.8	$23.7\ (0.999)^{k}$	−3.3	24.3	−4.11	36,63,64
22	$RC_6H_4NH_2$ **3f,h,j,k,m,p** + 2,4-$(NO_2)_2C_6H_3Cl$ **24**	EtOH	6	318	$37.7\ (0.999)^{k}$	$60.4\ (0.999)^{k}$	19.2	$18.4\ (0.999)^{k}$	22.3	15.4	−3.06	9, 36, 64
23	$RC_6H_4NH_2$ **3h,j,m** + 2,4,6-$(NO_2)_3C_6H_2Cl$ **25**	C_6H_6	3	298	$27.0\ (0.956)^{k}$	−2.0	−0.6	$27.6\ (0.996)^{k}$	−0.7	27.7	−4.79	36, 65
Acyl-transfer reactions												
24	$RC_6H_4NH_2$ **3c,h,j,y,z** + PhCOCl **26**	C_6H_6	5	298	$14.7\ (0.986)^{k}$	0	0	$14.7\ (0.992)^{k}$	0	14.7	−2.90	35,66,67
25	$RC_6H_4NH_2$ **3h,j,y,z** + PhCOCl **26**	Et_2O	4	298	$19.1\ (0.999)^{k}$	14.4	4.3	$14.8\ (0.994)^{k}$	5.3	13.8	−2.84	35,67

Table 1 (*continued*)

Entry	Reactants	Solvent	N[a]	T/K[b]	$\delta\Delta H^{\ddagger}$/kJ mol^{-1} σ^{-1} $(r)^{c,d}$	$\delta\Delta S^{\ddagger}$/J mol^{-1} K^{-1} σ^{-1} $(r)^{c,d}$	$T\ \delta\Delta S^{\ddagger}$/kJ mol^{-1} σ^{-1}	$\delta\Delta G^{\ddagger}$/kJ mol^{-1} σ^{-1} $(r)^{c,d}$	$\delta\Delta H^{\ddagger}_{ext}$/kJ mol^{-1} σ^{-1e}	$\delta\Delta H^{\ddagger}_{int}$/kJ mol^{-1} σ^{-1f}	ρ^{c}	Ref.
26	$RC_6H_4NH_2$ **3h,m,z** + PhOCOCl **27**	MeCN	3	298	15.3 (0.937)	11.6	3.5	11.8 (0.999)	4.3	11.0	−2.22	35,68
27	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + PhCH=CHCOCl **28**	C_6H_6	6	298	17.1 (0.992)	−2.7	−0.8	17.9 (0.998)	−1.0	18.1	−2.77	69
28	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + 2-C_4H_3O–CH=CH–COCl **29**	C_6H_6	6	298	16.2 (0.990)	−6.4	−1.9	18.1 (0.998)	−2.4	18.6	−2.86	69
29	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + 2-C_4H_3S–CH=CH–COCl **30**	C_6H_6	6	298	16.8 (0.995)	−2.3	−0.7	17.5 (0.999)	−0.8	17.6	−2.74	69
30	$RC_6H_4NH_2$ **3b,c,f,h,j,m,z** + 3-C_4H_3S–COCl **31**	C_6H_6	7	298	17.5 (0.995)	−2.0	−0.6	18.1 (0.996)	−0.7	18.2	−3.21	70
31	$RC_6H_4OH{\cdot}K_2CO_3$ **8b,c,f** + PhC(O)OC_6H_3–$(NO_2)_2$-2,4 **32**	DMF	3	293	−0.25 (0.993)	−34.0 (0.999)	−10.0	9.7	−12.6	12.4	−1.72 (−2.15)[m]	35,71
32	$RC_6H_4OH{\cdot}K_2CO_3$ **8j,p,z** + PhC(O)OC_6H_3–$(NO_2)_2$-2,4 **32**	DMF	3	293	−10.2 (0.999)	−40.1 (0.999)	−11.7	1.5	−14.8	4.6	−0.36 (−0.87)[m]	35,71
33	$RC_6H_4OH{\cdot}K_2CO_3$ **8w,y,z** + PhC(O)OC_6H_3–$(NO_2)_2$-2,4 **32**	DMF	3	293	−7.0 (0.999)	−45.5 (0.999)	−13.3	6.3	−16.8	9.8	−1.14 (−1.72)[m]	35,71

[a] Number of compounds. [b] Temperature of experiments. [c] σ constants[12] were used in the correlation equations $\Delta H^{\ddagger} = \delta\Delta H^{\ddagger}\sigma + \Delta H_0^{\ddagger}$, $\Delta S^{\ddagger} = \delta\Delta S^{\ddagger}\sigma + \Delta S_0^{\ddagger}$, $\Delta G^{\ddagger} = \delta\Delta G^{\ddagger}\sigma + \Delta G_0^{\ddagger}$ and $\log k = \rho\sigma + \log k_0$; standard errors of the $\delta\Delta H^{\ddagger}$, $\delta\Delta S^{\ddagger}$ and $\delta\Delta G^{\ddagger}$ reaction constants are estimated to be less than 9%, 12% and 7%, respectively. [d] Values given without correlation coefficient are calculated by the equation $\delta\Delta G^{\ddagger} = \delta\Delta H^{\ddagger} - T\ \delta\Delta S^{\ddagger}$. [e] Values are calculated by the equation $\delta\Delta H^{\ddagger}_{ext} = T_{comp}\delta\Delta S^{\ddagger}$, where $T_{comp} = 370$ K. [f] $\delta\Delta H^{\ddagger}_{int} = \delta\Delta H^{\ddagger} - \delta\Delta H^{\ddagger}_{ext}$. [g] Value is calculated for compounds **1c,f,h,z**. [h] Value is calculated for compounds **3c,j,m**. [i] Value is calculated for compounds **3b,c,h,m**. [j] Value is calculated for compounds **3c,f,j,k,n**. [k] σ^{-} constants[12] were used in the correlations. [l] Value is calculated by eqn (10). [m] Value is calculated by eqn (15).

following nucleophilic attack with the formation of a σ-complex through the transition state $\mathbf{TS_2}$ (Scheme 3).[36] Moreover, the activation free energies, $\Delta G^{\ddagger}$, for these reactions approach the $\Delta G^{\ddagger}$ range for one's without the preliminary **IC** step (entries 15, 16, 21–23). (Fig. 2). Therefore, the reason for deviations in Fig. 2 is an appreciable reduction of the $\delta\Delta S^{\ddagger}$ reaction constants for these reactions due to the stronger solvation of the transition states $\mathbf{TS_2}$ (Scheme 3).[36,71]

On the basis of the solvation theory developed by Hepler,[23,24] values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are divided into internal (ΔH_{int}, ΔS_{int}) and external (ΔH_{ext}, ΔS_{ext}) terms, referring to the chemical reactions and the solvation process, respectively.[23,24,27] In the same way the $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ reaction constants of this paper can be divided also into internal and external parts [eqn (11) and (12)].[28–36]

$$\delta\Delta H^{\ddagger} = \delta\Delta H^{\ddagger}_{int} + \delta\Delta H^{\ddagger}_{ext} \qquad (11)$$

$$\delta\Delta S^{\ddagger} = \delta\Delta S^{\ddagger}_{int} + \delta\Delta S^{\ddagger}_{ext} \qquad (12)$$

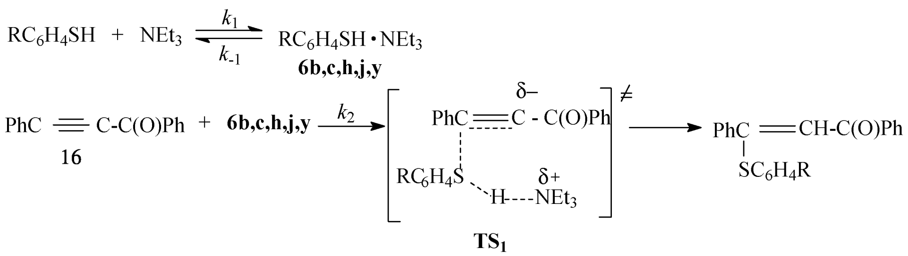
The changes in the $\delta\Delta S^{\ddagger}$ values caused by the variation of the remote substituent on the aromatic ring result from the changes in solvation (external term $\delta\Delta S^{\ddagger}_{ext}$). Therefore, it is possible to believe, that in the eqn (12) the internal part of the activation entropy is independent of the substituent in the absence of a steric effects ($\delta\Delta S^{\ddagger}_{int} \approx 0$) and $\delta\Delta S^{\ddagger} \approx \delta\Delta S^{\ddagger}_{ext}$.[23,24,27,42,46] In this case, the magnitude of $\delta\Delta H^{\ddagger}_{ext}$ can be calculated by the eqn (13).[23–27,42,46]

$$\delta\Delta H^{\ddagger}_{ext} = T_{comp}\delta\Delta S^{\ddagger} \qquad (13)$$

In this equation the T_{comp} value corresponds to the compensation temperature[42,46] amounting to 370 for reactions as described by the eqn (10). It should be noted that the intercept in eqn (10) is the $\delta\Delta H^{\ddagger}_{int}$ value for the given reaction series which varies only very slightly with the remote substituents on the aromatic ring. The values of $\delta\Delta H^{\ddagger}_{ext}$ and $\delta\Delta H^{\ddagger}_{int}$ calculated from eqn (11) and (13) are given in Table 1. Values $\delta\Delta H^{\ddagger}_{int}$ are always positive for all reactions excluding the reactions of entry 10 in Table 1. In this case, the value of $\delta\Delta H^{\ddagger}_{int}$ is negative and close to zero.

The sign of $\delta\Delta H^{\ddagger}_{ext}$ depends on the difference in solvation of initial reagents and corresponding transition states, as well as on $\delta\Delta S^{\ddagger}_{ext}$ or $\delta\Delta S^{\ddagger}$: if $\delta\Delta H^{\ddagger}_{ext} > 0$ (entries 1, 8, 10, 11, 12, 15, 16, 22, 25, 26 in Table 1), stronger solvation of initial reagents on passing to electron-withdrawing substituents R leads to increase in the magnitudes of $\delta\Delta H^{\ddagger}_{ext}$. Negative values of $\delta\Delta H^{\ddagger}_{ext}$ imply increased solvation of the corresponding transition states and a reduction in the magnitudes of $\delta\Delta H^{\ddagger}_{ext}$ upon introduction of electron-withdrawing substituents R (entries 2–7, 9, 13, 17–21, 23, 27–33 in Table 1) (*cf.* ref. 30, 32 and 35–37).

As implied by the data for the S_N2,[47] S_NAr[36] and acyl-transfer reactions[35] the reaction constants $\delta\Delta G^{\ddagger}$ and $\delta\Delta H^{\ddagger}_{int}$ become very close for the majority of reaction series and a linear dependences between these constants are supported. An analysis of the $\delta\Delta H^{\ddagger}_{int}$ and $\delta\Delta G^{\ddagger}$ values from Table 1 shows that these values are close for reactions of entries 1–4, 6–13, 15, 16 and 21–30. A linear relationship (14) between $\delta\Delta H^{\ddagger}_{int}$ and $\delta\Delta G^{\ddagger}$ for the reactions of these entries has been developed (Fig. 3). The intercept in eqn (14) is the $\delta\Delta G^{\ddagger}_{ext}$ value and close



Scheme 2 Ad_N reactions of compound **16** with nucleophiles **6** in toluene.

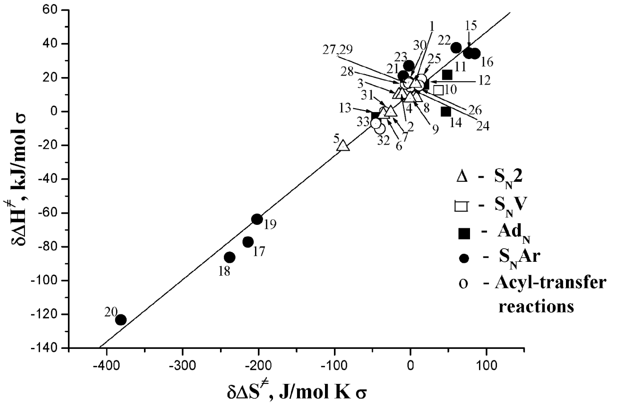


Fig. 1 Plot of $\delta\Delta H^{\ddagger}$ *vs.* $\delta S^{\ddagger}$ for the S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions of compounds **9–32** with anionic and neutral nucleophiles **1–8** in various solvents; the identity of the numbers is the entry number in Table 1.

to zero: $\delta\Delta G^{\ddagger}_{ext} = \delta\Delta H^{\ddagger}_{ext} - T\,\delta\Delta S^{\ddagger}_{ext} \approx 0$.[28–34,46] The latter means that the dependence of the free energy of activation is governed mainly by the changes in the internal enthalpy of activation of the chemical reaction: $\delta\Delta G^{\ddagger} \approx \delta\Delta H^{\ddagger}_{int}$.[11,28–34,46] It is obvious that realisation of dependence (14) becomes possible, as the substituent effects on the changes of the $\delta\Delta H^{\ddagger}_{int}$ values are similar for the BNR for which the k_1 (entries 10–13, 15, 16, 21–23) or k_c (entries 1–4, 6–9, 24–30) step is presumed to be rate-determined (Scheme 1).

$$\delta\Delta H^{\ddagger}_{int} = (-1.2 \pm 0.6) + (1.07 \pm 0.04)\delta\Delta G^{\ddagger};\quad r = 0.982,\ s = 1.3,\ n = 24 \qquad (14)$$

However, some concerted reactions (entry 5 in Table 1; Fig. 3) noticeably deviate from the dependence (14). The reason for this deviation, possibly, is an appreciable reduction of the $\delta\Delta G^{\ddagger}$ constants for these reactions. The latter is connected with a larger change of an entropy component at formation of a transition state. The S_N2 reactions of entry 5, possibly, involve the formation of the cyclic transition state **TS$_3$** (Scheme 4). Usually, the formation of the cyclic transition state is accompanied by a lower values of activation entropy.[17,77]

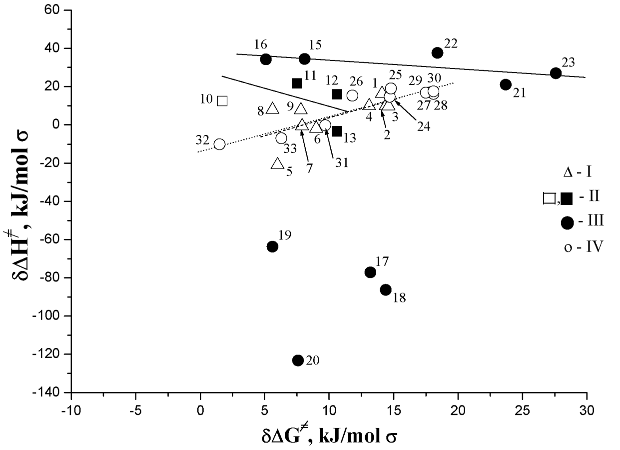


Fig. 2 Plots of $\delta\Delta H^{\ddagger}$ *vs.* $\delta\Delta G^{\ddagger}$ for the S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions of compounds **9–32** with anionic and neutral nucleophiles **1–8** in various solvents; the identity of the numbers is the entry number in Table 1.

Taking into account the fact that according to the Hammett equation the $\delta\Delta G^{\ddagger}$ reaction constant can be determined as $\delta\Delta G^{\ddagger} = -2.303RT\rho$[9,32] and considering the relationship of eqn (14), a correlation (15) between $\delta\Delta H^{\ddagger}_{int}$ and ρ for the reactions of entries 1–4, 6–13, 15, 16 and 21–30 (for which the k_c or k_1 step is presumed to be rate-determining) has been developed as shown in Table 1 and Fig. 4.

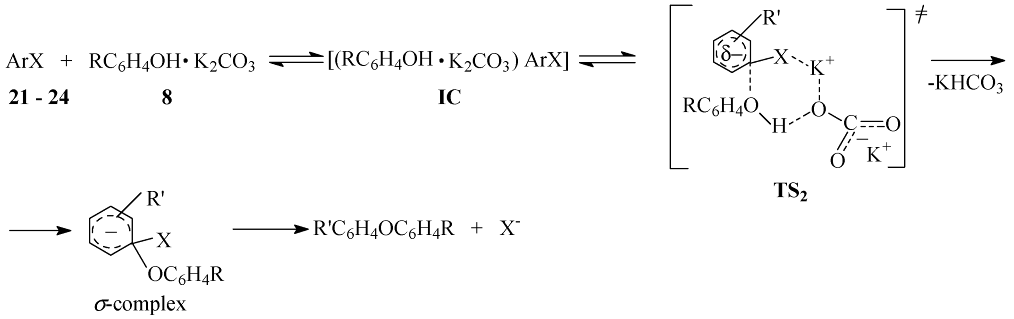
$$\delta\Delta^{\ddagger}_{int} = (-0.7 \pm 0.8) - (6.1 \pm 0.3)\rho;\quad r = 0.971,\ s = 1.6,\ n = 24 \qquad (15)$$

Realisation of this dependence becomes possible, as magnitudes of $\rho(k_c)$ or $\rho(k_1)$ for these reactions characterise charge development at the transition state of the concerted and stepwise

Table 2 The compensation relationships $\delta\Delta H^{\ddagger}$ *vs.* $\delta\Delta S^{\ddagger}$ for some bimolecular nucleophilic substitution and addition reactions with the substituents R in the nucleophiles

Reaction kind	Equation[a]	*r*	*s*	*n*	Ref.
S_N2	$\delta\Delta H^{\ddagger} = (11.1 \pm 1.5) + (0.35 \pm 0.04)\delta\Delta S^{\ddagger}$	0.947	3.8	9	47
Ad_N	$\delta\Delta H^{\ddagger} = (9.4 \pm 1.2) + (0.27 \pm 0.03)\delta\Delta S^{\ddagger}$	0.994	2.0	3	—[b]
S_NAr	$\delta\Delta H^{\ddagger} = (12.7 \pm 4.0) + (0.38 \pm 0.02)\delta\Delta S^{\ddagger}$	0.988	10.4	9	36
Acyl-transfer reactions	$\delta\Delta H^{\ddagger} = (15.2 \pm 1.4) + (0.49 \pm 0.06)\delta\Delta S^{\ddagger}$	0.944	3.9	10	—[b]

[a] Values of $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ are taken from Table 1. [b] Present work.



Scheme 3 S_NAr reactions of compounds **21–24** with nucleophiles **8** in DMF.

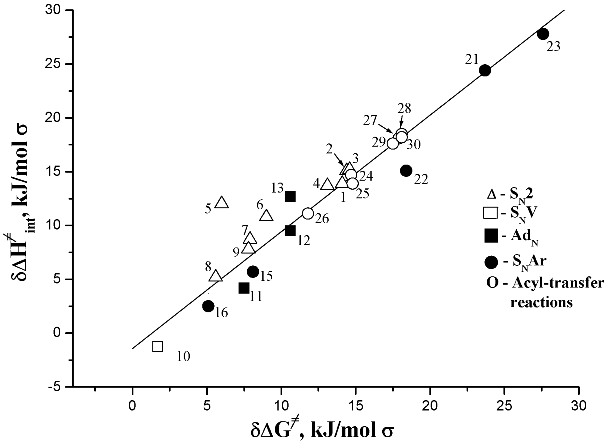
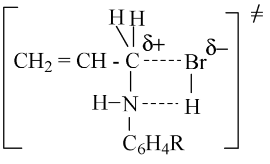


Fig. 3 Plots of $\delta\Delta H^{\ddagger}_{int}$ *vs.* $\delta\Delta G^{\ddagger}$ for the S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions of compounds **9–32** with anionic and neutral nucleophiles **1–8** in various solvents; the identity of the numbers is the entry number in Table 1.



TS$_3$

Scheme 4 Proposed structure of transition state **TS$_3$** for the reactions of entry 5 in Table 1.

processes (Scheme 1).[11,38–40] Therefore, for reactions of entry 5 the value of $\rho(k_c)$ has been calculated by the eqn (15) using the $\delta\Delta H^{\ddagger}_{int}$ value (Table 1; Fig. 4). The calculated value of $\rho(k_c)$ (entry 5) differs significantly from values ρ, obtained by the Hammett equation with the use of observable rate constants for these reactions (Table 1).[47,52] In the case of the reactions of entry 5 the calculated magnitude of $\rho(k_c)$ relates to the concerted mechanism with frontside (S_N2-f) attack by nucleophile at the α-carbon of the substrate through the **TS$_3$** in comparison with the same mechanism with backside attack (S_N2-b) (Schemes 1 and 4).[17,77] It is evident that the deviation of the ρ value from the eqn (15) can be explained by the contribution of both attacking ways.

Eqn (15) has been used to calculate the $\rho(k_2)$ values for the Ad_N reactions of entry 14 through the **TS$_1$** (Scheme 2). At the same time the calculated magnitude of ρ_{eq} (k_1/k_{-1}) for the formation of nucleophiles **6b,c,h,j,y** is positive and equal to 4.77 (Scheme 2).

The deviations of the ρ values from eqn (15) for the S_NAr reactions of entries 17–20 were connected with the formation of the intermediate complex **IC** (Scheme 3).[36,61,62] Therefore, for these reactions the values of $\rho(k_1)$ calculated by eqn (15) (Table 1) were used to calculate the ρ_{eq} values from $\rho = \rho_{eq} + \rho(k_1)$ for a step of formation of **IC** (Scheme 3).[36] These magnitudes are negative or positive and equal to −1.21, −1.43, 1.04 and 2.04 for reactions of entries 17–20 in Table 1, respectively.[36]

As for the deviations of the acyl-transfer reactions of entries 31–33 (Table 1) from the dependence (15), these reactions are stepwise with the decomposition of the intermediate $\mathbf{T}^{\pm}$ as a rate-limiting step (Scheme 1).[35,71] Therefore, for reactions of entries 31–33 the values $\rho(k_1)$ have been calculated by the eqn (15) for the reaction step forming the intermediate $\mathbf{T}^{\pm}$ using the $\delta\Delta H^{\ddagger}_{int}$ values (Table 1). Then, the ρ and $\rho(k_1)$ values were used to calculate the magnitudes of $\rho(k_2/k_{-1})$ for the step corresponding to decomposition of intermediate $\mathbf{T}^{\pm}$ from $\rho = \rho(k_1) + \rho(k_2/k_{-1})$. These magnitudes are positive and equal to 0.43, 0.38 and 0.50 for reactions of entries 31–33 in Table 1, respectively (*cf.* ref. 35).

It is obvious from the relationship of eqn (15) that the $\delta\Delta H^{\ddagger}_{int}$ reaction constant, as well as the reaction constant

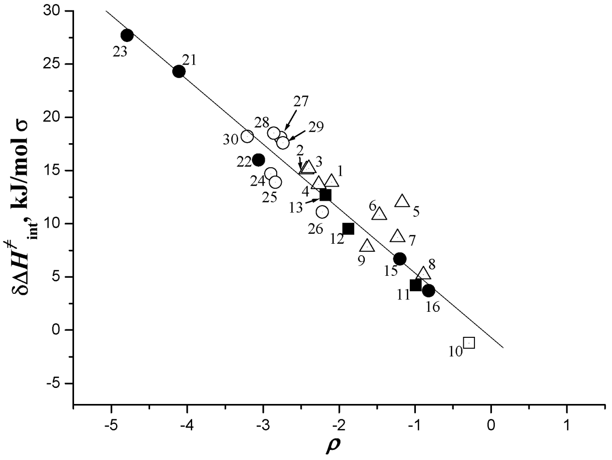


Fig. 4 Plots of $\delta\Delta H^{\ddagger}_{int}$ *vs.* ρ for the S_N2, S_NV, Ad_N, S_NAr and acyl-transfer reactions of compounds **9–32** with anionic and neutral nucleophiles **1–8** in various solvents; the identity of the numbers is the entry number in Table 1.

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ρ from the Hammett equation,[9,11,37–41] characterizes the degree of developing negative charge in the transition states (rate constants k_c or k_1 on Scheme 1). The large absolute values of $\delta\Delta H^{\ddagger}_{\mathrm{int}}$ indicate essential charge development in the transition state of $\mathrm{S_NAr}$ reactions of entries 21 and 23 (Fig. 4). Though the correlation dependence (15) cannot provide a basis for assignment of a stepwise or concerted reaction mechanism, nevertheless this relationship equally well describes those reactions which proceed by both mechanisms. Since in the stepwise reactions with rate-limiting formation of an intermediate the deviations from the dependence (15) are absent, some deviations observed can be explained by a realisation of alternative ways for these reactions.

Conclusions

Determining the compensation dependence between the $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values in the $\mathrm{S_N2}$, $\mathrm{S_NV}$, $\mathrm{Ad_N}$, $\mathrm{S_NAr}$ and acyl-transfer reactions for variations of substituents at the nucleophiles gives a straightforward way of estimating T_{comp} and obtaining $\delta\Delta H^{\ddagger}_{\mathrm{int}}$.

The $\delta\Delta H^{\ddagger}_{\mathrm{int}}$ values give a single linear dependence with the values of ρ from the Hammett equation for all BNR proceeding by a concerted mechanism and a stepwise mechanism through an intermediate with its formation being the rate-determining step. It is evident that the deviations from dependence of $\delta\Delta H^{\ddagger}_{\mathrm{int}}$ *vs.* ρ can be interpreted in terms of a change of transition state structure or reaction mechanism.

References

1 M. B. Smith and J. March, *March's Advanced Organic Chemistry*, Wiley, New York, 6th edn, 2007.
2 S. S. Shaik, H. B. Schlegel and S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry, the S_N2 Mechanism*, Wiley, New York, 1992.
3 A. Pross, *Theoretical and Physical Principles of Organic Reactivity*, Wiley, New York, 1995.
4 E. Buncel, J. M. Dust and F. Terrier, *Chem. Rev.*, 1995, **95**, 2261.
5 C. F. Bernasconi and Z. Rappoport, *Acc. Chem. Res.*, 2009, **42**, 993.
6 C. F. Bernasconi, *Tetrahedron*, 1989, **45**, 4017.
7 A. Williams, *Concerted Organic and Bio-organic Mechanisms*, CRC Press, Boca Raton, FL, 2000.
8 E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, CA, 2006.
9 J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, London, 1963.
10 V. M. Vlasov, *Russ. Chem. Rev.*, 2006, **75**, 765.
11 C. D. Johnson, *The Hammett Equation*, Cambridge University Press, 1973.
12 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
13 T. M. Krygowski and B. T. Stępień, *Chem. Rev.*, 2005, **105**, 3482.
14 M. Palusiak and T. M. Krygowski, *New J. Chem.*, 2009, **33**, 1753.
15 K. C. Westaway and Z. Waszczylo, *Can. J. Chem.*, 1982, **60**, 2500.
16 W. K. Kim, W. S. Ryu, I.-S. Han, C. K. Kim and I. Lee, *J. Phys. Org. Chem.*, 1998, **11**, 115.
17 H. K. Oh, J. H. Yang, H. W. Lee and I. Lee, *New J. Chem.*, 2000, **24**, 213.
18 G. R. Cowie, H. J. M. Fitches and G. Kohnstam, *J. Chem. Soc.*, 1963, 1585.
19 B. A. Shainyan, *Russ. Chem. Rev.*, 1986, **55**, 511.
20 H. J. Koh, K. L. Han and I. Lee, *J. Org. Chem.*, 1999, **64**, 4783.
21 H. K. Oh, M. H. Ku, H. W. Lee and I. Lee, *J. Org. Chem.*, 2002, **67**, 3874.
22 H. J. Koh, K. L. Han, H. W. Lee and I. Lee, *J. Org. Chem.*, 2000, **65**, 4706.
23 L. G. Hepler, *J. Am. Chem. Soc.*, 1963, **85**, 3089.
24 L. G. Hepler, *Can. J. Chem.*, 1971, **49**, 2803.
25 T. M. Krygowski and W. R. Fawcett, *Can. J. Chem.*, 1975, **53**, 3622.
26 T. M. Krygowski and W. R. Fawcett, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2033.
27 T. M. Krygowski and J. Guillemé, *J. Chem. Soc., Perkin Trans. 2*, 1982, 531.
28 A. Fábián, F. Ruff and Ö. Farcas, *J. Phys. Org. Chem.*, 2008, **21**, 988.
29 F. Ruff and Ö. Farcas, *J. Phys. Org. Chem.*, 2008, **21**, 53.
30 F. Ruff and Ö. Farcas, *J. Org. Chem.*, 2006, **71**, 3409.
31 F. Ruff, Ö. Farcas and Á. Kucsman, *Eur. J. Org. Chem.*, 2006, 5570.
32 F. Ruff, *Internet Electron. J. Mol. Des.*, 2004, **3**, 474.
33 F. Ruff, *THEOCHEM*, 2003, **625**, 111.
34 F. Ruff, *THEOCHEM*, 2002, **617**, 31.
35 V. M. Vlasov, *New J. Chem.*, 2009, **33**, 501.
36 V. M. Vlasov, *J. Phys. Org. Chem.*, 2009, **22**, 756.
37 O. A. El Seoud, M. Ferreira, W. A. Rodrigues and M.-F. Ruasse, *J. Phys. Org. Chem.*, 2005, **18**, 173.
38 C. F. Bernasconi, M. E. Z. Michoff, R. H. de Rossi and A. M. Granados, *J. Org. Chem.*, 2007, **72**, 1285.
39 C. F. Bernasconi, M. Pérez-Lorenzo and S. J. Codding, *J. Org. Chem.*, 2007, **72**, 9456.
40 Y. Kondo, M. Urade, Y. Yamanishi and X. Chen, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1449.
41 D. R. Edwards, P. Montoya-Peleaz and C. M. Crudden, *Org. Lett.*, 2007, **9**, 5481.
42 L. Liu and Q. X. Guo, *Chem. Rev.*, 2001, **101**, 673.
43 W. Linert, *Chem. Soc. Rev.*, 1994, **23**, 429.
44 W. Linert and R. F. Jameson, *Chem. Soc. Rev.*, 1989, **18**, 477.
45 O. Exner, *Chem. Commun.*, 2000, 1655.
46 O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411.
47 V. M. Vlasov, *J. Phys. Org. Chem.*, DOI: 10.1002/poc.1634.
48 Q.-g. Li and Y. Xue, *J. Phys. Chem. A*, 2009, **113**, 10359.
49 D. P. Evans, H. B. Watson and R. Williams, *J. Chem. Soc.*, 1939, 1345.
50 T. Matsui and N. Tokura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1751.
51 E. M. Arnett and R. Reich, *J. Am. Chem. Soc.*, 1980, **102**, 5892.
52 T. J. Rao, G. Punnaiah and E. V. Sundaram, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1986, **97**.
53 I. Lee, H. J. Koh, B. C. Lee and B. S. Park, *Bull. Korean Chem. Soc.*, 1994, **15**, 576.
54 S. P. Saksena and A. N. Bose, *Indian J. Chem.*, 1975, **13**, 421.
55 B. A. Shainyan and A. N. Mirskova, *Zh. Org. Khim. (Russ.)*, 1980, **16**, 2569.
56 B. Varghese, S. Kothari and K. K. Banerji, *Int. J. Chem. Kinet.*, 1999, **31**, 245.
57 B. Varghese, S. Kothari and K. K. Banerji, *J. Chem. Res. (M)*, 1998, 1853.
58 N. V. Korzhova, V. S. Pisareva and S. P. Korshunov, *Zh. Org. Khim. (Russ.)*, 1975, **11**, 1030.
59 N. V. Korzhova, S. P. Korshunov, V. E. Statsyuk and I. V. Bodrikov, *Izv. Vysh. Uchebn. Zaved., Khim. Khim. Tekhnol. (Russ.)*, 1982, **25**, 813.
60 A. A. El-Bardan, *J. Phys. Org. Chem.*, 1999, **12**, 347.
61 I. A. Khalfina and V. M. Vlasov, *Russ. J. Org. Chem.*, 2005, **41**, 978.
62 I. A. Khalfina and V. M. Vlasov, *J. Phys. Org. Chem.*, 2007, **20**, 369.
63 A. W. Chapman and R. E. Parker, *J. Chem. Soc.*, 1951, 3301.
64 R. E. Parker and T. O. Read, *J. Chem. Soc.*, 1962, 9.
65 L. M. Litvinenko, I. G. Sipovatka, T. S. Skoropisova and S. V. Ostrovskaya, *Ukraina Khim. Zh.*, 1959, **25**, 189.
66 E. G. Williams and C. N. Hinshelwood, *J. Chem. Soc.*, 1934, 1079.
67 E. Tommila and T. Vihavainen, *Acta Chem. Scand.*, 1968, **22**, 3224.
68 K. H. Yew, H. J. Koh, H. W. Lee and I. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2263.
69 G. Alberghina, A. Arcoria and S. Fisichella, *J. Org. Chem.*, 1978, **43**, 1122.

70 A. Arcoria and S. Fisichella, *J. Org. Chem.*, 1973, **38**, 3774.
71 I. A. Khalfina and V. M. Vlasov, *Russ. J. Org. Chem.*, 2008, **44**, 1619.
72 A. R. Stein, M. Tencer, E. A. Moffatt, R. Dawe and J. Sweet, *J. Org. Chem.*, 1980, **45**, 3539.
73 R. R. Krug, W. G. Hunter and R. A. Grieger, *J. Phys. Chem.*, 1976, **80**, 2335.
74 R. R. Krug, W. G. Hunter and R. A. Grieger, *J. Phys. Chem.*, 1976, **80**, 2341.
75 O. V. Kulikov, P. V. Lapshev and I. V. Terekhova, *Russ. J. Phys. Chem.*, 1998, **72**, 725.
76 D. H. Leung, R. G. Bergman and K. N. Raymond, *J. Am. Chem. Soc.*, 2008, **130**, 2798.
77 I. Lee, *Chem. Soc. Rev.*, 1990, **19**, 317.