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Linear Free Energy Relationships in S_NAr Reactions of Aryl and Diaryl *N*-Anions with Aryl Halides

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Abstract—A good correlation has been established between the Brønsted coefficients β_{Nuc} and β_{ox} for reactions of aryl-containing *N*-anions with various aryl halides. This correlation reflects the dependence of the internal barrier of aromatic nucleophilic substitution on the oxidation potentials of nucleophiles.

Nucleophilic substitution is an actively studied class of reactions widely used in organic synthesis. Elucidation of factors controlling the reactivity of *N*-anions in nucleophilic substitution is a topical problem in view of both quantitative evaluation of the nucleophilic reactivity and development of methods of functionalization of aromatic amines with the aim to prepare monomers, antioxidants, drug preparations, dendrimers, etc. [1–3].

To characterize the reactivity of aryl-containing *N*-anions, it is important to know the mechanisms of reactions with their participation. Presently, the question as to whether aromatic nucleophilic substitution can proceed by the single electron transfer (*SET*) mechanism is actively discussed [4–9].

There are several approaches to prediction of the probability of passing from S_N2 or S_NAr to *SET* mechanism. In one of them, the Marcus equation is used to estimate the *SET* rate constants of the reactions of anions with 33 different electrophiles, including aryl halides. Then the theoretical k_{SET} values are compared with the experimental rate constants k_{exp}, to estimate the probability of the *SET* mechanism [10, 11]. Another approach is based on comparison of the nucleophilic substitution rate with the rate constants of the reactions for which the *SET* mechanism is well established [12]. One more well-known approach is to analyze the coefficients in the Edwards equation (1) [13, 14].

$$\log k/k_0 = \alpha E_n + \beta H, \tag{1}$$

where k and k_0 are the rate constants; E_n and H, oxidation potential and basicity of a nucleophile; and α and β, constants reflecting the sensitivity of the reaction rate to changing oxidation potential and basicity of the nucleophile, respectively.

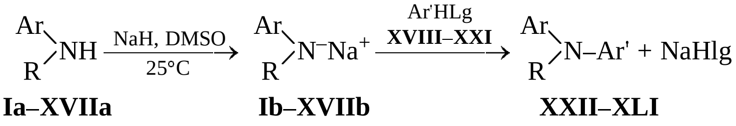
Previously it was demonstrated [15, 16] that S_N2 reactions proceed by the *SET* mechanism if $\beta_{\mathrm{Nuc}} \sim 1$. In this work we propose an approach to predicting the probability of passing from S_NAr to *SET*, based on analysis of the relationship between the Brønsted coefficients β_{Nuc}, determined from the dependence of the logarithm of the rate constant $\log k$ on pK of the starting NH acids for the reactions of aryl halides with *N*-anions, and the constants of proportionality β_{ox} determined from Eq. (2) for the same reactions.

$$\log k = \beta_{\mathrm{ox}} E_{\mathrm{ox}} + c, \tag{2}$$

where E_{ox} is the oxidation potential of *N*-anion.

We believe that such an analysis allows prediction of the probability of the *SET* mechanism at $\beta_{\mathrm{Nuc}} \sim 1$. Scheme 1 represents the route of the reaction of *N*-anions **Ib**–**XVIIb**, prepared from amines **Ia**–**XVIIa**, with aryl halides **XVIII**–**XXI**.

Scheme 1.



See table for Ar, Ar', and R.

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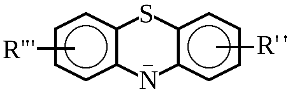
p*K* of **Ia–XVIIa**, rate constants *k* of reactions of *N*-anions **Ib–XVIIb** with aryl halides in DMSO at 25°C, Brønsted coefficients β_{Nuc}, oxidation potentials E_{ox} of *N*-anions **Ib–XVIIb**, and coefficients β_{ox} found from log k–E_{ox} relationships for the same reactions

No.	Nu⁻ series	p*K*[a]	E_{ox}, V[b]	Reaction product ArN(R)Ar'	*k*,[c] l mol⁻¹ s⁻¹	β_{Nuc}	$-\beta_{ox}$
1	ArNH⁻	Ar'Hlg : C_6F_6 **XVIII**, –1.76[d]		R = H, Ar' = C_6F_5		0.74 [17] (*r* 0.998, *s* 0.13, *n* 5)	9.36 [18] (*r* 0.982, *s* 0.44, *n* 4)
	Ar = C_6F_5 **Ib**	23.1	–0.09	**XI**	4.4×10 [15]		
	Ar = $4\text{-}NO_2C_6H_4$ **IIb**	21.5	0.05	**XXII**	3.0 [15]		
	Ar = $4\text{-}C_5F_4N$ **IIIb**	19.2	0.44	**XII**	4.2×10^{-2} [15]		
	Ar = $1,4\text{-}NO_2C_{10}H_6$ **IVb**	18.0	0.24	**XXIII**	1.1×10^{-2} [15]		
	Ar = 4-CNC6F4 **Vb**	17.9	0.36	**XXIV**	5.4×10^{-3} [15]		
2		Ar'Hlg : $1\text{-}F\text{-}4\text{-}NO_2C_6H_4$ **XX**, –1.08[d] [19]		Ar' = $4\text{-}NO_2C_6H_4$		0.51 [20]	6.81 (*r* 0.952, *s* 0.29, *n* 3)
	R'' = R''' = H **VIb**	22.7 [20]	-0.209^e	**XXV**	9.4×10^{-1} [20]		
	R'' = 2-Cl, R''' = H **VIIb**	20.79 [20]	-0.035^e	**XXVI**	9.3×10^{-2} [20]		
	R'' = 3-Br, R''' = 7-Br **VIIIb**	20.13 [20]	-0.05^e	**XXVII**	4.5×10^{-2} [20]		
3	ArN–Ar''	Ar'Hlg : C_5F_5N **XIX**, –1.63[d]		Ar' = $4\text{-}C_5F_4N$		0.34 (*r* 0.986, *s* 0.16, *n* 4)	3.92 (*r* 0.990, *s* 0.14, *n* 4)
	Ar = Ph, Ar'' = $4\text{-}C_5F_4N$ **IXb**	15.1	0.29	**XXVIII**	1.7×10^{-1}		
	Ar = C_6F_5, Ar'' = $4\text{-}CH_3C_6F_4$ **Xb**	13.3	0.43	**XXIX**	8.4×10^{-2}		
	Ar = Ar'' = C_6F_5 **XIb**	12.6	0.48	**XXX**	3.1×10^{-2}		
	Ar = C_6F_5, Ar'' = $4\text{-}C_5F_4N$ **XIIb**	9.4	0.78	**XXXI**	2.3×10^{-3}		
4	PhN–Ar	Ar'Hlg : $1\text{-}F\text{-}4\text{-}NO_2C_6H_4$ **XX**, –1.08[d] [19]		Ar' = $4\text{-}NO_2C_6H_4$		0.24 [21] (*r* 0.997, *s* 0.12, *n* 4)	4.00 [18] (*r* 0.990, *s* 0.22, *n* 4)
	Ar = Ph **XIIIb**	25.5	–0.38	**XXXII**	3.3×10^{-1} [15]		
	Ar = $3\text{-}Cl\text{-}C_6H_4$ **XIVb**	24.1	–0.23	**XXXIII**	2.1×10^{-1} [15]		
	Ar = $4\text{-}NO_2C_6H_4$ **XVb**	17.45	0.13	**XXXIV**	3.5×10^{-3} [15]		
	Ar = $4\text{-}CNC_6F_4$ **XVIb**	14.7	0.28	**XXXV**	1.2×10^{-3} [15]		
5	ArNH⁻	Ar'Hlg : $1\text{-}F\text{-}4\text{-}NO_2C_6H_4$ **XX**, –1.08[d] [19]		R = H, Ar' = $4\text{-}NO_2C_6H_4$		0.28 [21] (*r* 0.985, *s* 0.14, *n* 4)	3.93 [18] (*r* 0.995, *s* 0.09, *n* 3)
	Ib	23.1	–0.09	**II**	1.4×10^{-1} [18]		
	IIb	21.5	0.05	**XXXVI**	3.0×10^{-2} [18]		
	IIIb	19.2	0.44	**XXXVII**	7.6×10^{-3} [18]		
	IVb	17.9	0.28	**XXXVIII**	4.8×10^{-3} [18]		
6	ArNH⁻	Ar'Hlg : $1\text{-}Cl\text{-}4\text{-}NO_2C_6H_4$ **XXI**, –1.08[d] [19]		R = H, Ar' = $4\text{-}NO_2C_6H_4$		0.26 [22] (*r* 0.996, *s* 0.07, *n* 4)	3.84 [18] (*r* 0.999, *s* 0.009, *n* 3)
	Ib	23.1	–0.09	**II**	$1.1\times10^{-1\,f}$ [22]		
	IIb	21.5	0.05	**XXXVI**	$3.3\times10^{-2\,f}$ [22]		
	IIIb	19.2	0.44	**XXXVII**	$1.1\times10^{-2\,f}$ [22]		
	IVb	17.9	0.28	**XXXVIII**	$4.3\times10^{-3\,f}$ [22]		
7	ArN⁻Ar''	Ar'Hlg : C_6F_6 **XVIII**, –1.76[d]		Ar' = C_6F_5		0.14 (*r* 0.980, *s* 0.12, *n* 4)	1.73 (*r* 0.985, *s* 0.11, *n* 4)
	XVb	17.45	0.13	**XXXIX**	2.5×10^{-3}		
	XVIb	14.7	0.28	**XL**	1.5×10^{-3}		
	Ar = C_6F_5, Ar'' = $4\text{-}ClC_6F_4$ **XVIIb**	12.0	0.53	**XLI**	3.7×10^{-4}		
	XIIb	9.4	0.78	**XXX**	2.1×10^{-4}		

[a] 9-Phenylfluorene was used as a reference [17]; [b] against the standard calomel electrode [18], [c] standard deviation was within 15%, [d] reduction potential E_{red} (V) of aryl halides in DMSO against the standard calomel electrode (supporting electrolyte tetraethylammonium perchlorate), [e] against the standard hydrogen electrode [11], and [f] at 60°C.

Characteristics of the reactants, reactions, and products are summarized in the table.

Steric hindrance in *N*-anions strongly affects β_{Nuc}. Analysis of series nos. 2 and 4 (see table) shows that, over the same basicity range, the steric hindrances decrease on passing from the *N*-anions of diarylamines **XIIb**–**XVIb** to cyclic phenothiazinide ions **VIb**–**VIIIb**, and β_{Nuc} considerably increases [21]. The β_{Nuc} values for the reactions of *N*-anions of aryl- and diarylamines with aryl halides were found to be from 0.14 to 0.74, which is beyond the ordinary β_{Nuc} range in S_NAr reactions [23]. It should be pointed out that this range includes the β_{Nuc} values reported by Bordwell for the reactions of phenothiazinide anions with *p*-nitrofluorobenzene (β_{Nuc} 0.51) and *p*-nitrochlorobenzene (β_{Nuc} ~0.70) [20], the latter value being approximate, as obtained by averaging of two experimental values. Evidently, in contrast to S_N2 reactions, in which β_{Nuc} is practically constant for different *N*-anions (0.32–0.33) [24], in the case of the reactions of *N*-anions with aryl halides, β_{Nuc} may change considerably, as a result of increasing steric hindrance in formation of the transition state of the S_NAr reaction.

It is known that the coefficient β_{Nuc} is a measure of the sensitivity of the rate constant to variations in the basicity of a nucleophile. Its value reflects the degree of charge transfer and binding in the transition state of the rate-determining stage of the reaction [25, 26]. Furthemore, for *N*-anions of similar basicities, β_{Nuc} increases with increasing electrophilicity of the substrate. For example, for the reactions of a series of *N*-anions of similar basicities with pentafluoropyridine (**XIX**), β_{Nuc} is higher by 0.2 than that for the reaction with less electrophilic hexafluorobenzene (**XVIII**) (nos. 3, 7), and β_{Nuc} for the reactions of *N*-anions **Ib**–**Vb** with hexafluorobenzene (**XVIII**) is higher by 0.46 than that for the reaction of the same *N*-anions with *p*-nitrofluorobenzene (**XX**) (nos. 1, 5). It should not be expected that the nature of the leaving group considerably affects β_{Nuc} in S_NAr reactions, since even in S_N2 reactions, where the bond with the leaving group is broken in the rate-determining stage, such an effect was not observed. Indeed, the dependence of β_{Nuc} on the nature of the leaving group is insignificant (nos. 5, 6), and the rate constants of these reactions decrease on passing from F to Cl, suggesting that the investigated S_NAr reactions (Scheme 1) proceed by the addition–elimination mechanism through the formation of an intermediate σ complex as a rate-determining stage [20, 27].

Therefore, β_{Nuc} increases with decreasing steric hindrance in a nucleophile and increasing electrophilicity of a substrate. For the investigated S_NAr reactions, β_{Nuc} can be as large as 0.74 but not unity. In *SET* reactions, the charge is entirely transferred, and β_{Nuc} ~1 [15, 16].

Previously we have established good correlations between the logarithms of the rate constants of S_NAr reactions of arylamine and diarylamine *N*-anions with aryl halides and the reduction potentials of these anions [18]. The slopes β_{ox} of these dependences are given in the table (nos. 1–7). Analysis of the β_{ox} values for the reactions of *N*-anions **IXb**–**XIIb** and **XVb**–**XVIIb** with compounds **XIX** and **XVIII** (nos. 3, 7) shows that β_{ox} increases with increasing electrophilicity of a substrate. The rates of *SET* reactions are mostly independent of the steric effects in a nucleophile [11, 28]. In reactions with the same electrophile, *p*-nitrofluorobenzene, β_{ox} increases on passing from diarylamine *N*-anions **XIIIb**–**XVIb** to phenothiazinide anions **VIb**–**VIIIb** (nos. 4, 2). Cyclic anions **VIb**–**VIIIb**, making weaker steric hindrance to electrophilic attack [21], are characterized by higher β_{ox}. This gives an additional evidence in favor of the fact that the reactions under consideration proceed by the S_NAr but not *SET* mechanism. Since the coefficient β_{ox} characterizes the sensitivity of the rate constant to variation of the oxidation potential of the nucleophile, its value can be used to estimate the probability for the *SET* mechanism to occur: the higher the absolute value of β_{ox}m, the higher the probability of an *SET* reaction. It is well known that the *SET* mechanism is quite probable in the case of very readily oxidizable nucleophiles or very readily reducible electrophiles [11, 12, 29]. Comparison of the reduction potentials E_{red} of **XVIII** and **XX** (nos. 1, 5) shows that the easier reduction of **XX** as compared to **XVIII** does not result in increase in the absolute value of β_{ox} in the latter case, demonstrating once more that the reactions under consideration proceed by the S_NAr but not *SET* mechanism.

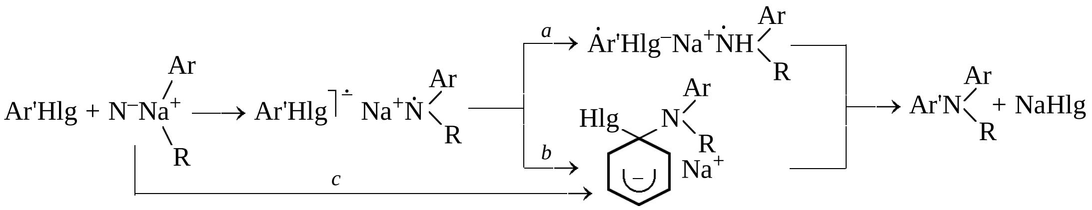
Therefore, the same factors influence β_{Nuc} and β_{ox}, and a higher β_{Nuc} corresponds to a higher absolute value of β_{ox} (see table). We have established a good correlation (3) between β_{Nuc} and β_{ox} for several series of *N*-anions (see figure).

$$\beta_{Nuc} = -0.03 - 0.08\beta_{ox};\ r\ 0.985,\ s\ 0.04\ n\ 7. \quad (3)$$

The scatter of data observed in the figure for compounds $ArN^{-}Ar''$ and $PhN^{-}Ar$ (point nos. 3 and 4) can be attributed to the fact that the stabilizing effects in radicals $ArN^{\cdot}Ar''$ (point no. 3) are weaker than those in $PhN^{\cdot}Ar$ radicals (point no. 4) [18].

At β_{Nuc} ~1, β_{ox} was estimated by Eq. (3) to be about –12.8, which is close to β_{ox} = –12.0 reported for the reaction of phenothiazinide ions with 1,1-dinitrocyclohexane [11]. The β_{ox} values of –17.5 and –14.2 were reported for the *SET* reactions of 9-substituted fluorenide ions with 1-*p*-tolylsulfonyl-1-nitrocyclohexane and 1,1-dinitrocyclohexane, respectively [30, 31]. For the *SET* reaction of 9-substituted fluorenide ions with 2-iodo-1,1,1-trifluoroethane, the dependence of log k_{exp} on the reduction potentials of anions $E_{ox}(A^-)$ gives β_{ox} = –8.7 [28]. Decreased β_{ox} in the latter case ca be explained by the possibility for the reaction to proceed by both the *SET* and S_N2 mechanisms. As seen from Scheme 2, *N*-anions can react with aryl halides by three mechanisms: chain *SET* (route *a*) [32, 33], nonchain *SET* (route *b*) [34], and S_NAr (route *c*) [6, 20, 27].

Scheme 2.



The arguments against route *a* are as follows: the observed second-order kinetics, the lack of radical dimerization products, the effect of steric hindrance in a nucleophile on β_{ox} (nos. 4, 2), and independence of β_{ox} from the reduction potential of an electrophile (nos. 1, 5). Most likely, *N*-anions react with aryl halides through formation of an intermediate σ complex. Such a σ complex can be formed by nonchain single electron transfer followed by recombination of the resulting radical with a radical anion (Scheme 2, route *b*) [34] or by the S_NAr mechanism (Scheme 2, route *c*) [6, 20, 27]. It is difficult to decide between routes *b* and *c*, because they are kinetically indistinguishable. Solution of this problem requires further investigation of the reactions of aryl halides with readily ozidizable *N*-anions by, for example, the radical clock method [35]. Appropriate *N*-anions can be selected using β_{ox} at β_{Nuc} ~1.

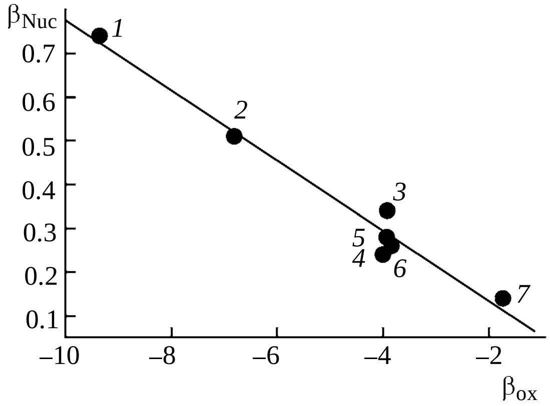
Thus, both the theoretical and experimental β_{ox} values for the *SET* reactions of *N*-centered anionic nucleophiles (–12.8 and –12.0) are lower in the absolute value than the experimental β_{ox} values found for similar reactions of carbanions with electron acceptors (–17.5 and –14.2 [30, 31]). This is probably due to more positive oxidation potentials of *N*-anions as compared to carbanions of equal basicity, as a result of higher electronegativity of the nitrogen atom [11]. It is clearly seen that, at $\beta_{Nuc} = -a\beta_{ox} + b$ and β_{Nuc} ~1, the slope *a* is 0.06 and 0.08 for the *SET* reactions of carbanions and *N*-anions, respectively [11]. These *a* values are close to that in Eq. (3). Therefore, Eq. (3) can be considered as a general relationship relating both coefficients (β_{Nuc} and β_{ox}) to each other and allowing prediction of the probability for a reaction to proceed by the *SET* mechanism. Obviously, the coefficients α and β in Eq. (1) can be related to each other also.

As known, β_{Nuc} can be derived from the Marcus equation (4) [36] by differentiation with respect to ΔG^0 using Eq. (5).

$$\Delta G^{\neq} = \Delta G_0^{\neq} + 1/2\Delta G^0 + (\Delta G^0)^2/16\Delta G_0^{\neq}, \quad (4)$$

$$\beta_{Nuc} = 1/2 + \Delta G^0/8\Delta G_0^{\neq}. \quad (5)$$

Here $\Delta G^{\neq}$ and ΔG^0 are the activation and reaction free energies, respectively, and $\Delta G_0^{\neq}$ is the internal barrier. Equations (4) and (5) interrelate β_{Nuc} and $\Delta G_0^{\neq}$, but not β_{ox} and $\Delta G_0^{\neq}$. Therefore, comparison of Eqs. (3) and (5) is the first case when the internal barrier of a reaction ($\Delta G_0^{\neq}$) is related to the oxidation potential of a nucleophile.



β_{Nuc}–β_{ox} correlation for the reactions of *N*-anions **Ib–XVIIb** with aryl halides **XVIII–XXI** in DMSO; numbering of the points corresponds to that in the table.

EXPERIMENTAL

Synthesis and purification of compounds **IX**–**XII** and **XV**–**XVII** are described elsewhere [18, 37]. Compounds **XVIII** and **XIX** were commercial chemicals. Reaction products **XXVIII**–**XXXI** and **XXXIX**–**XLI** were isolated and characterized by NMR and IR spectra. Their melting points and spectroscopic characteristics are well consistent with the reference data [38, 39]. Dimethyl sulfoxide was vacuum-distilled at 10^{-3}–10^{-4} mm Hg from CaH_2. Commercial sodium hydride (20% suspension in silicone oil) was washed twice with anhydrous hexane and dried in an oven under flowing argon to remove traces of the solvent.

The reduction potentials of **XVIII** and **XIX** were determined on an LP-7e polarograph using a standard three-electrode cell against a saturated calomel electrode. The working and auxiliary electrodes were made from Pt wire. The working electrode was renewed by firing in a torch flame. Cyclic voltammograms were recorded in DMSO under Ar at 83 mV s^{-1} sweeping rate (temperature 25°C, supporting electrolyte 0.1 M Et_4NClO_4). The irreversible peak potentials E_{red} of **XVIII** and **XIX** given in the table are close to the reference data [29, 40].

All determinations of the rate constants were performed under Ar. Diarylamines **IX**–**XII** and **XV**–**XVII** and aryl fluorides **XVIII** and **XIX** were taken in the equimolar amounts [concentrations $(3–6) \times 10^{-2}$ M]; and a threefold excess of sodium hydride was taken relative to the amount of a diarylamine. The rate constants were determined by potentiometric titration using a lanthanum fluoride electrode [41]. Weighed portions of the compounds in spherical glass ampules ~10 mm in diameter were evacuated to 10^{-4} mm Hg and placed into an all-soldered glass system. The solvent was introduced and degassed by freeze–pump–thaw cycles in a vacuum. Then the system was evacuated to 10^{-4} mm Hg and sealed off the vacuum line. By successively breaking the ampules with a glass ball, we initially generated the *N*-anion and then conducted the reaction for a fixed time, quenching it by adding a weighed portion of 65% HNO_3. Then the reaction mixture was diluted with water and transferred into a 50-ml volumetric flask. From data on the fluoride concentration, we estimated the second-order rate constant by the equation

$$k = [2.303/\tau(a - b)]\log[b(a - x)/a(b - x)],$$

where a and b are the initial reactant concentrations (M); x is the product concentration (M); and τ, reaction time (s). The rate constants for the reactions of **XVIII** with *N*-anions **XIIb** and **XVb**–**XVIIb** were estimated using a statistical factor $k' = k/6$ for the equivalent positions realized with **XVIII**. The estimated rate constants were reproducible to within ±15%; no less than three replicate runs were performed.

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